Electrochemical Investigation of Liquid Amalgams of Thallium, Indium, Tin, Zinc, Cadmium, Lead, Copper, and Lithium.

BY

THEODORE WILLIAM RICHARDS

WITH THE COLLABORATION OF

J. HUNT WILSON AND R. N. GARROD-THOMAS.

PUBLISHED BY THE
CARNEGIE INSTITUTION OF WASHINGTON
1909

CARNEGIE INSTITUTION OF WASHINGTON
PUBLICATION No. 118

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE

The Lord Baltimore Press
BALTIMORE, MD., U. S. A.

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I.

Electrochemical Investigation of Liquid Amalgams of Thallium, Indium, and Tin.

By Theodore W. Richards and J. Hunt Wilson.

INTRODUCTION.

The change in free energy during a chemical reaction may be regarded as composed of at least two separate quantities, one which may be said to be due to the affinities involved in the reaction, the other depending upon the relative concentration of initial substances and products. The calculation of the magnitudes of these quantities is a matter of prime importance, for free energy is the driving agency of all earthly things. Unfortunately the actual determination of changes of free energy is only possible in the case of easily reversible reactions, and these form a comparatively small part of many examples of chemical change.

Of great theoretical importance in this connection are the reversible galvanic cells, which involve in their action simply the dilution of liquid amalgams, and consequently suffer no appreciable change of heat capacity. The study of such cells can furnish much light upon the second of the two independent quantities which together constitute the total free energy of a reaction, namely, concentration effect. Von Türin pointed out the analogy between such cells and the concentration elements first investigated by Helmholtz and offered the first consistent theory of amalgam cells. G. Meyer measured cells of this type, but much more accurate data have been obtained at Harvard University. The object of this recent work, which concerned itself with cells containing zinc and cadmium amalgams over a considerable range of concentration, was to test the application of the gas law to solutions of this type, as well as to apply the equations of Helmholtz and of Cady to the data. Great accuracy was sought. Since the two metals presented widely different phenomena, and since both of these metals are bivalent, it seemed desirable to extend the work by measuring similar cells, employing a wide variety of other metals with other valencies. In this way a more complete survey of the possibilities would certainly be obtained.

This monograph embodies the results of the further investigation of amalgam cells, containing not only the two metals already mentioned, but also thallium, indium, tin, lead, copper, and lithium. The first section of the monograph deals with thallium, indium, and tin. These metals are especially interesting because they are respectively univalent, trivalent, and (under some conditions) quadrivalent. Thallium is, moreover, interesting in its chemical behavior, having in common with the alkali-metals a soluble hydroxide, carbonate, and sulphate, while on the other hand resembling lead in the possession of an insoluble chromate and sulphide, and a slightly soluble chloride. Indium is the only trivalent metal that forms satisfactory amalgams for the present purpose.[1]

The effort was made to attain precision sufficient to afford an adequate basis for the desired theoretical considerations. No attempt was made to attain the greatest conceivable precision, because such an attempt would have defeated the object of the investigation, by so limiting the variety of results obtainable in the limited time as to have restricted their generalization.

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[1] An almost complete historical review may be found in the monograph of Richards and Forbes (Publication of Carnegie Institution of Washington, No. 56; Zeitschrift für phys. Chem., **58**, 683 [1907]). A paper by J. Regnauld (Compt. Rend., **53**, 533 [1861]) on the heat of amalgamation of the metals was overlooked in this review, and the date of Helmholtz's publication (Monatsbericht d. kgl. pr. Akad., Berlin, 1877, p. 713) was accidentally given as 1882 instead of 1877. The reference to Lindeck's work is Wied. Ann., **35**, 311, 1888. Mention should be made of a mathematical paper by Trevor on the "Electromotive Force of Concentration Cells" (Zeitschr. Elektrochem., **11**, 681 [1905]). While this paper contains interesting features, experimental verification of the equation deduced therein is not possible at present. In a recent paper published after most of the work embodied in this monograph had been completed, Carhart discusses the Helmholtz equation, as applied to amalgam cells. (Phys. Rev., March, 1908). In a yet more recent paper by Hulett and De Lury, published after the conclusion of the present work, the work of Richards and Forbes is in part repeated and extended to more dilute solutions. In so far as the two investigations overlap, they confirm one another (J. Am. Chem. Soc., **30**, 1812 [1908]). Another theoretical paper, by van Laar (Arch. Néerl. d. Sci. ex. et nat. [II] VIII, 296), should perhaps be mentioned.

VALUES OF CONSTANTS.

In the discussion which follows, all the experimental work is viewed in the light of three mathematical expressions:

$$\pi = \frac{U}{\nu F} + T\frac{d\pi}{dT} \qquad (1)$$

$$\pi = \frac{RT}{\nu F} ln \frac{c_1}{c_2} \qquad (2)$$

$$\pi = \frac{U}{\nu F} + \frac{RT}{\nu F} ln \frac{c_1}{c_2} \qquad (3)$$

In these expressions,

π = electromotive force.
F = Faraday's equivalent = 96,530 coulombs.
R = the gas constant.
T = the absolute temperature.
ν = valence.
ln = natural logarithm to the base e.
c_1 = concentration of more concentrated amalgam.
c_2 = concentration of less concentrated amalgam.
U = the change of total energy involved in the dilution of the amalgam.

The first of the numbered equations is the well-known expression of Helmholtz (sometimes called the Gibbs-Helmholtz equation); the second contains the substance of the proposal of von Türin and G. Meyer; and the third is the suggestion of Cady and Lewis. Both of the last two may be said to be the outcome of other work of Helmholtz, and to be covered by the equation of Nernst. Before defining the quantities whose symbols are given in the foregoing list, it may be well to say a word about these fundamental equations themselves.

Equation (1) needs no comment. Equation (2) has been reached in somewhat different ways by a number of thinkers; it is based essentially upon the epoch-making discussion by Helmholtz of the concentration cell.[2] The forms in which the several investigators have expressed their results appear to be different, although they express essentially the same idea; the equation, as given here, is not exactly like that of any of them. Nernst,[3] who did not himself at first apply his equation to cells of the type under consideration, used the ratio of pressures instead of the ratio of concentrations, and would have expressed the result thus

$$\pi = \frac{RT}{\nu F}\left(ln \frac{P}{p} - ln \frac{P'}{p}\right)$$

[2] Helmholtz, Monatsberichte d. kgl. pr. Akad., Berlin, 1877, p. 713. Helmholtz's other well-known paper on the thermodynamic equation numbered (1) above was published in the Sitzungsberichte der kgl. pr. Akad., Berlin, in February, 1882, p. 22.
[3] Nernst, Zeitschr. phys. Chem., **4**, 129 (1889).

In this equation P and P' represent the unknown solution-pressures, whose ratio alone is to be inferred, and p the osmotic pressure of the appropriate ion in the electrolyte. The latter cancels, being common to both electrodes, and the expression becomes $\pi = \frac{RT}{\nu F} ln \frac{P}{P'}$. If no other source of free energy other than osmotic effect is present, $\frac{P}{P'}$ may be taken as equal to $\frac{c_1}{c_2}$ and the equation reduces to ours. In this expression the absence of association in the dissolved metal is assumed. Both Nernst's expression and that given above are calculated on the basis of the gram-atom.

On the other hand, von Türin [4] and Meyer [5] expressed their equations in terms of concentration, and calculated them on the basis of the electrochemical equivalent in terms of grams per coulomb; and both introduced the molecular weight (M or μ) of the dissolved metal—although, to be sure, von Türin seems to have accidentally omitted this quantity from his final statement.[6] Their equation, reached in different ways, reads [7]

$$\pi = \frac{q}{M} 19.1 T \log_{10} \frac{c_1}{c_2} = \frac{q}{M} 8.32 T \left(2.303 \log_{10} \frac{c_1}{c_2} \right) = \frac{q}{M} RT ln \frac{c_1}{c_2}$$

Bearing in mind the fact that their q meant $\frac{gram\text{-}atomic\ weight}{\nu F}$ and that we have made the additional assumption (based upon the measurements of many investigators) that M = gram-atomic weight, it is seen that their form is essentially identical with that given above. Our form will be called in future merely "the concentration-equation," as its ascription to any one author might under the circumstances seem invidious.

Attention should be called to the fact that Helmholtz, himself, insisted that his original concentration-equation holds true only when there is no heat of dilution involved in the reaction,[8] a condition reiterated by von Türin. The same limitation applies, of course, to the equation in its present simplified form; but this limitation does not necessarily apply to the equation of Nernst, involving solution-pressures instead of concentrations. The term solution-pressure must be interpreted as including combined effect of all the tendencies affecting the escape of the dissolved metal from

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[4] von Türin, Zeitschr. phys. Chem., **5**, 340 (1890); **7**, 221 (1891).

[5] G. Meyer, Zeitschr. phys. Chem., **7**, 447 (1891).

[6] See von Türin on the bottom of page 221, Zeitschrift für physikalische Chemie, **7** (1891).

[7] By a coincidence of misprints, of which there are many in the papers of both von Türin and Meyer, the decimal point of the factor 19.1 has been misplaced in each case and reads 1.91. This mistake was inadvertently copied in reporting the history of their work in Publication 56 of the Carnegie Institution of Washington.

[8] Helmholtz, Berliner Monatsbericht, November, page 713 (1877).

the amalgam, except the osmotic pressure of the ion dissolved in the electrolyte. Thus P and P' include the effect of the chemical free energy change connected with dilution; and if such exists $\frac{P}{P'}$ can not be equal to $\frac{c_1}{c_2}$. This explanation appears to be necessary, because of the misconception of Carhart concerning the significance of the Nernst equation.[9]

The equation of Cady[10] and of Lewis[11] is an attempt to take account of the heat of dilution, thus resolving the tendencies P and P' into their most important components. This equation may only be supposed to hold true when there is no change of heat capacity during the reaction. Further explanation may be deferred until the present research has been described, when a still more recent suggestion of Lewis, concerning the application of the law of Raoult $\left(\frac{\Delta p}{p} = \frac{n}{N+n}\right)$ to osmotic work, will also be considered.

Before beginning a description of our experimental work it will be well to consider the accuracy with which the various quantities in the equations are defined.

In a previous contribution from this laboratory[12] the results of Rayleigh,[13] F. and W. Kohlrausch,[14] Kahle,[15] and Patterson and Guthe,[16] concerning the value of Faraday's equivalent F, have been compared; and the conclusion was reached that 96,580 coulombs are associated with 107.93 grams of silver, if the silver is weighed in a form free from mother-liquor, after having been deposited in a manner avoiding anode complications. The more recent work of Smith, Mather and Lowry, and others, has not changed our opinion on this point.[17] Since Richards, Collins and Heimrod,[18] and Richards and Stull[19] have established the universality of Faraday's law on a firmer basis than ever, the same value can be used for a gram equivalent of thallium or indium with reasonable accuracy. If the atomic weight of silver is taken as 107.88, a value probably nearer the

[9] H. S. Carhart, Phys. Rev., **26,** 216 (1908).
[10] Cady, Journ. Phys. Chem. **2,** 551 (1898).
[11] Lewis, Proc. Am. Acad. **35,** 34 (1899).
[12] Proc. Amer. Acad., **37,** 415 (1902).
[13] Phil. Trans., **175,** 411 (1884).
[14] Wied. Ann., **27,** 1 (1886).
[15] Wied. Ann., **67,** 1 (1889).
[16] Phys. Rev., **7,** 257 (1898).
[17] Smith, Mather and Lowry, Phil. Trans. Roy. Soc. London, Series A, **207,** 545 (1908); also see especially T. W. Richards, Proc. Am. Acad., **44,** 91 (1908). The Report of the International Conference on Electrical Units and Standards, "Science," **28** (1908), recommends F = 96,540 for the same atomic weight without these precautions. This probably amounts to about the same thing.
[18] Zeit. phys. Chem., **32,** 301 (1900).
[19] Proc. Amer. Acad., **35,** 123 (1899).

truth, the value F must be diminished by 0.05 per cent, and becomes 96,530 coulombs per gram equivalent. This latter value is used in the work which follows, and all atomic weights also are referred to this standard.

The symbol ν represents the valency of the metallic ion in the electrolyte of the cell. Since thallous sulphate and indium sulphate were used as electrolytes in the cells of thallium and indium amalgams, it is difficult to conceive how the valency of the ions of thallium and indium could be other than 1 and 3 respectively. The valency of tin will receive especial consideration when that metal is discussed; in our experiments it was undoubtedly 2, not 4.

The work of Daniel Berthelot [20] probably affords the most accurate value of R, which we may express conveniently in mayers. A mayer is the heat capacity which is warmed 1 degree centigrade by 1 joule. According to Berthelot's work, the space occupied by a gram-molecule of a perfect gas at 760 mm. pressure, 45° latitude at the sea-level, may be taken as 22.412 liters (the atomic weight oxygen being 16.000), and the absolute zero at −273.08° C. These values are probably accurate at least to within 0.05 per cent. The value of R on this basis will be

$$R=\frac{76.00\times 13.596\times 980.6\times 22{,}412}{273.08\times 10^{7}}=8.316 \text{ mayers.}$$

T, by which R is multiplied in the formula, is the temperature of the cell referred to the hydrogen scale. This was fixed in our experiments by means of four exactly known thermometers. Over the range of temperature employed in the following measurements these readings are closely comparable with the corresponding thermodynamic temperatures. Moreover, the experimental determination of the temperature to within 0.01° would fix the value of $\frac{T_1}{T_0}$ within one part in 30,000, a degree of accuracy far greater than can be attained with the rest of the data used in calculating the electromotive forces.

It appears, then, that the values of ν, R, T, and F are known with considerable accuracy, and it now remains to consider the concentration ratio $\frac{c_1}{c_2}$. An error of 0.1 per cent in this ratio would cause an error of 0.00001 volt in the electromotive force, and it is clear that the early investigators have not determined this ratio with sufficient accuracy. If a weight w of amalgam of concentration c_1 is mixed with a weight nw of mercury to form a new amalgam of concentration c_2, it is not permissible in accurate work to write

$$\frac{c_1}{c_2}=n+1$$

[20] Trav. et Mém. du Bureau internat. des poids et mesures, **13**, 113 (1903).

as seems to have been the custom of previous workers in this field. Richards and Forbes have shown the necessity of applying a correction for the difference in density of the two amalgams being compared. For example, let w be the weight of an amalgam of concentration c_1 diluted with w_{Hg} grams mercury to form a new amalgam c_2. Now, if D_1 and D_2 are the densities of the amalgams, we have

$$\frac{c_1}{c_2} = \frac{v_2}{v_1} = \frac{\dfrac{w_1 + w_{Hg}}{D_2}}{\dfrac{w_1}{D_1}} = \frac{w_1 + w_{Hg}}{w_1} \times \frac{D_1}{D_2}$$

Careful determinations were made of the densities of the several amalgams at various concentrations; and corresponding corrections were applied to the calculated values of the concentration ratio. These determinations will be considered later in their proper place. The densities were all measured at 20°; their relative values undoubtedly change slightly with the temperature, but not enough to affect appreciably the calculation in question.

In calculating the thermochemical results, one 18° calorie was taken as equal to 4.181 joules.[21]

A number of typical cadmium standard cells, containing crystals of cadmium sulphate, prepared from different pure materials at different times, were used as the standard of electromotive force. As these all agreed within the tenth of a millivolt, their value was taken as

$$1.0184 - 0.00004\ (t° - 20°) \text{ international volts}$$

and this value was used as the standard of electromotive force.[22]

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[21] Callendar and Barnes, Phil. Trans., A, **199**, 149 (1902).

[22] See Report of International Conference on Electrical Units and Standards, 1908—published in many places, for example, "Science," **28**, 743 (1908).

PREPARATION OF THE AMALGAMS.

The thallous sulphate used in preparing the thallium amalgams was a sample which had been many times recrystallized, both as acid sulphate and as sulphate. The original preparation had been of a high grade of purity. The indium amalgams were prepared from a sample of very pure indium, which, through the kindness of Professor L. M. Dennis, of Cornell University, was available for this work.[23] The sample in question had been carefully purified for use in the determinations of the atomic weight of indium, although it was not the purest specimen used for this purpose, and was finally fused in a current of hydrogen. It contained no impurity, except a trace of iron. Metallic tin was obtained by the electrolysis of an acid solution of pure stannous chloride, using a pure carbon anode. The fine needles of tin were washed with distilled water and alcohol and dried in a desiccator over sulphuric acid.

Pure mercury was obtained as follows: Crude mercury was shaken first with sulphuric acid to remove the major part of the metallic impurities and then for some time with dilute nitric acid and mercurous nitrate. The sample was now wholly free from contamination with the more electropositive metals. It was then distilled under a pressure of 20 mm. of hydrogen in an apparatus somewhat similar to that described by Hulett.[24] The hydrogen was passed through three towers, containing solid potash, in order to purify and dry it. The entire apparatus, as far as the connection to the pump, was wholly fused together in order to avoid rubber connections or glass joints. The pipettes in which the mercury was kept were themselves used as the receivers of this still, and the mercury was sealed in them without for an instant coming in contact with the air. The stopcock, regulating the supply of gas bubbling through the mercury, was lubricated with sirupy phosphoric acid. The mercury thus obtained must have been very pure. Distillation in air, recommended by Hulett, affords an excellent means of oxidizing other metals present; but our experience leads us to fear that the product contains a trace of dissolved oxygen. Accordingly, we used hydrogen instead of air.

The water used in making up the solutions was distilled twice, first from an alkaline permanganate solution, and then from very dilute sulphuric acid.

Since amalgams of all the metals studied are very susceptible to oxidation, they were made and introduced into the measuring apparatus wholly out of contact with the atmosphere, and the mercury from which they were made was never allowed to come into contact with the air after its distillation in rarified hydrogen.

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[23] For details of purification of this indium see Jour. Amer. Chem. Soc., **29** (1907).
[24] Zeit. phys. Chem., **33,** 611 (1900).

It was found that the thallium amalgams could be most conveniently prepared by the electrolysis of a solution of thallous sulphate, using a mercury cathode. Addition of ammonium oxalate prevented the formation of peroxide on the anode. The complete apparatus used in preparing and transferring the amalgam is shown in fig. 1.

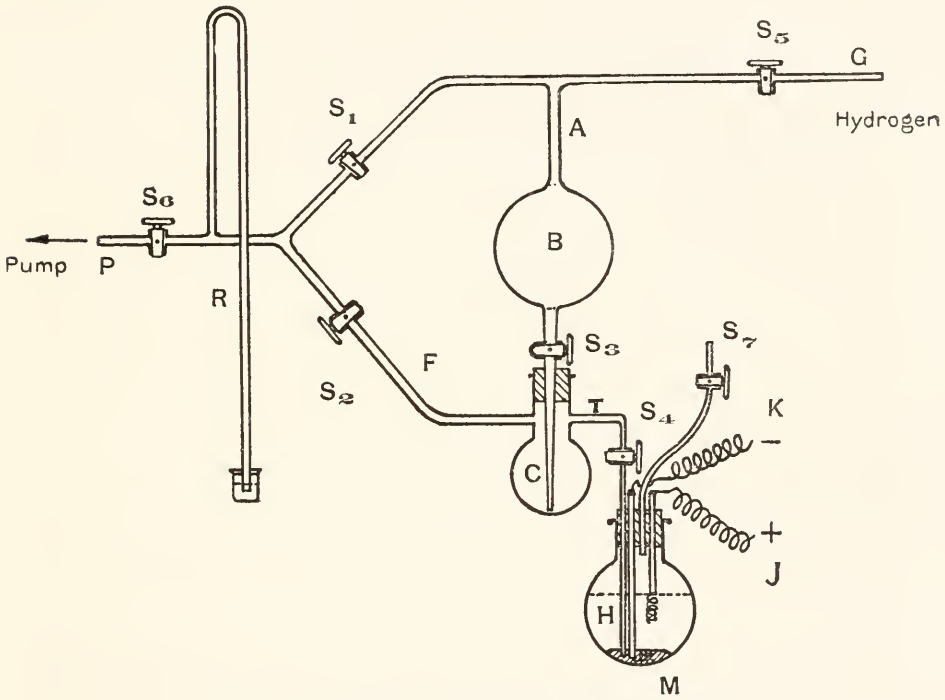

Fig. 1. Apparatus for Making and Preserving Amalgams.

The amalgams were prepared by electrolysis in the flask *H*. Connection was made to the mercury cathode by means of glass tube passing through the stopper carrying the wire *K*. The anode *J* terminated in a spiral of platinum wire. The anode was inclosed in a small linen bag (not shown in the figure), in order to prevent any peroxide which might be formed from falling on the cathode. The amount of thallium deposited was measured by a silver coulometer included in the circuit. The coulometer was of the form used by Richards and Heimrod. The porous cup was cleaned with concentrated nitric acid and then boiled with many portions of water before use. The anode was a bar of pure silver which had been prepared for use in an atomic weight research. Care was taken to keep the level of the liquid within the porous cup lower than that outside in order to prevent outward filtration. An amperemeter, also in the circuit, served for an approximate measurement of the current strength.

A weighed amount of pure mercury was run into the flask *H*, which was then nearly filled with a saturated solution of thallous sulphate containing about ten grams of ammonium oxalate. The stopper was inserted, care being taken that the cathode and the tube *T* leading to the flask *C* were immersed in the mercury. The current was now allowed to run until the desired quantity of thallium had been deposited. The time necessary for this could be calculated approximately from the readings on the amperemeter. On breaking the circuit, the amalgam was immediately sucked up into *C* by cautiously opening the stopcock S_4. The platinum crucible containing the deposited silver was washed with water, dried at 200°, and weighed. From the weight of the silver deposited, the concentration of the amalgam could be calculated.

The arrangement employed in transferring the amalgams was essentially similar to that used by Richards and Forbes. Hydrogen, prepared from pure hydrochloric acid and zinc, and purified by passing through four towers containing concentrated potassium hydroxide solution and dry fused potash, was supplied through the tube *G*. The pipette *B* communicated through *A* with either the hydrogen supply or the vacuum-pump. The outlet tube of *B*, terminating in a thick capillary, passed through a tightly fitting rubber stopper into the flask *C*. (The rubber stopper had been boiled with alkali, thoroughly washed with water and finally covered with soft paraffin.) The flask *C* was supplied with two side necks. The tube *F* communicated with the vacuum-pump, while *T* was bent down and passed to the bottom of the flask *H*.

The whole apparatus being thoroughly clean and dry, it was manipulated as follows: First S_4, S_1, and S_5 were closed and S_2 and S_3 were opened; the pressure in *B* and *C* was reduced to 15 mm. of mercury, and S_6 was closed. The manometer, *R*, proved that the apparatus was free from leakage. By cautiously opening S_5 the system was now filled with hydrogen; and the exhaustion and filling with hydrogen were repeated three or four times. Care was taken to expel the air in the capillary also by a stream of hydrogen. In order to force the hydrogen through the shallow layer of mercury in the bottom of *H*, the pressure in *H* was slightly diminished by suction through S_7. After the amalgam had been drawn up into *C*, a rapid stream of dry hydrogen was bubbled through it by opening S_5 and S_3, at the same time maintaining a low pressure in *C*. This served to dry the amalgam and to mix it thoroughly. After 10 or 15 minutes S_2 was closed and the system was allowed to fill with hydrogen. S_1 was then opened and *B* exhausted. By opening S_3 the amalgam could be drawn up into *B*. S_5 was finally opened and normal pressure restored in *B*, which was then sealed off at *A* by using a small blast flame. *F* was cut with a file and the flask *C* detached. The capillary tip of the pipette-

like tube of *B* was immediately sealed with wax to protect it from air. The pipettes were kept in a rack, shown in fig. 2.

Precisely the same mode of procedure was followed in preparing and protecting the electrolyte used in the cell. The stream of hydrogen was allowed to bubble through *C* for some time to remove the last traces of air from the solution. It was then drawn up into the pipette and sealed off as before. When the solution was wanted its weight was, of course, not sufficient to draw it out; accordingly the following method was used to follow it up with hydrogen: A clean rubber tube, delivering a stream of pure hydrogen, was slipped over the drawn-out portion, and the tube was then broken; in opening the stopcock, the solution readily flowed out.

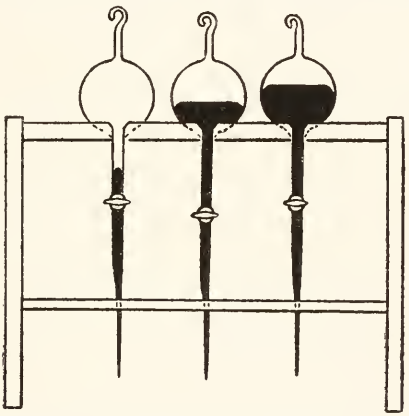

Fig. 2. Rack with Pipettes containing Amalgams.

The amalgams of indium and tin were prepared in the same apparatus. It was found more convenient to prepare the latter amalgams by adding the metals directly to the mercury in the atmosphere of carbon dioxide in the flask *H,* for they are far less readily oxidized than the others; but afterwards the amalgam was treated just as the others.

DENSITIES OF THE AMALGAMS.

It has been pointed out [25] that a knowledge of the densities of the various amalgams is essential in order to fix accurately the value of the concentration-ratio in calculating the theoretical potentials of the cells. Moreover, such data make possible the calculation of the contraction or expansion occurring on the amalgamation of the various metals. For these reasons numerous determinations were made of the densities of the amalgams of thallium, indium, and tin.

The pycnometer used was of the Sprengel type, as modified by Ostwald; its capacity was about 3 cc. and its tubes 1 mm. in diameter. Before use it was thoroughly cleaned with appropriate reagents, and, after washing with water, dried by suction. The weight of the pycnometer filled with mercury at 20° was then carefully determined. Since in filling the pycnometer with the amalgams, it was sometimes difficult to adjust the contents exactly to the marks, the weight of a centimeter length of mercury in the capillary was determined, and a suitable correction was applied. The length of any excess in the column of amalgam was accurately determined with dividers. Since the correction was small, never amounting to more than 0.15 gram, the difference in density between mercury and the amalgam would cause no appreciable error. All the densities were determined at 20°. The amalgams used in these determinations were prepared in the manner already described. When all was ready, a sufficient quantity of the amalgam was run out into a small weighing bottle, filled with carbon dioxide, and hastily drawn up into the pycnometer. By working in this fashion, no serious oxidation occurred. The thread of mercury was adjusted only after the pycnometer had been in a thermostat at 20.0° for some time.

The data of a typical determination are as follows:

Weight of pycnometer and mercury	53.228	Weight of pycnometer and amalgam	53.121
Weight of pycnometer alone	18.134	Weight of pycnometer alone	18.134
Weight of mercury	35.094	Weight of amalgam	34.987

The density of mercury at 20° is 13.545, therefore the density of the amalgam is

$$\frac{34.987}{35.094} \times 13.545 = 13.504$$

This amalgam contained 1.845 per cent thallium.

Table 1 contains the results with amalgams of thallium, indium, and tin. There are given also imaginary values which the densities would have shown if no contraction or expansion had taken place on amalgamation.

[25] Richards and Forbes, Publication of Carnegie Institution of Washington, No. 56, 11 (1906). Also, pp. 6 and 7 of the present monograph.

The values of the densities of the pure metals used for this calculation are given in the first column of the table. The value for the density of pure indium is the mean of two closely agreeing determinations made by us with Professor Dennis's pure sample of the metal, because the values previously obtained, 7.421 by Winkler and 7.12 by Thiel, are in very poor agreement. Our data are as follows:

First Determination:

Weight of pycnometer:	Grams.
With air-free water (20.0°)	10.1338
Alone	7.0012
With indium alone	10.2568
With indium and water	12.9420
Result: Density	7.277

Second Determination:

Weight of pycnometer:	
With indium alone	10.0045
With indium and water	12.7525
Result: Density	7.291

The mean value is 7.284. Corrected to vacuum the true density of indium is found to be 7.277.

TABLE I.—*Densities of Amalgams.*

Metal.	Per cent of solid metal in amalgam.	Correct weight of liquid needed to fill pycnometer.	Actual density of liquid.	Calculated imaginary density of amalgam.
Thallium (density 11.85)	1.854	34.987	13.504	13.509
	1.410	35.017	13.515	13.520
	0.793	35.049	13.527	13.530
Indium (density 7.28)	1.920	34.548	13.334	13.324
	1.430	34.703	13.394	13.380
	1.090	34.784	13.426	13.419
	0.928	34.835	13.446	13.439
	0.770	34.867	13.457	13.455
	0.468	34.949	13.489	13.490
Tin (density 7.29)	0.45	35.012	13.513	13.493
	0.30	35.027	13.519	13.510
	0.21	35.053	13.529	13.519
Mercury, pure (density 13.545)	0	35.095	13.545	13.545

The density curves for the thallium, indium, and tin amalgams are shown in fig. 3. The dotted lines give the imaginary values that would be obtained if neither expansion nor contraction took place on mixing. Indium and tin contract on amalgamation, while in the case of thallium there is a slight expansion.

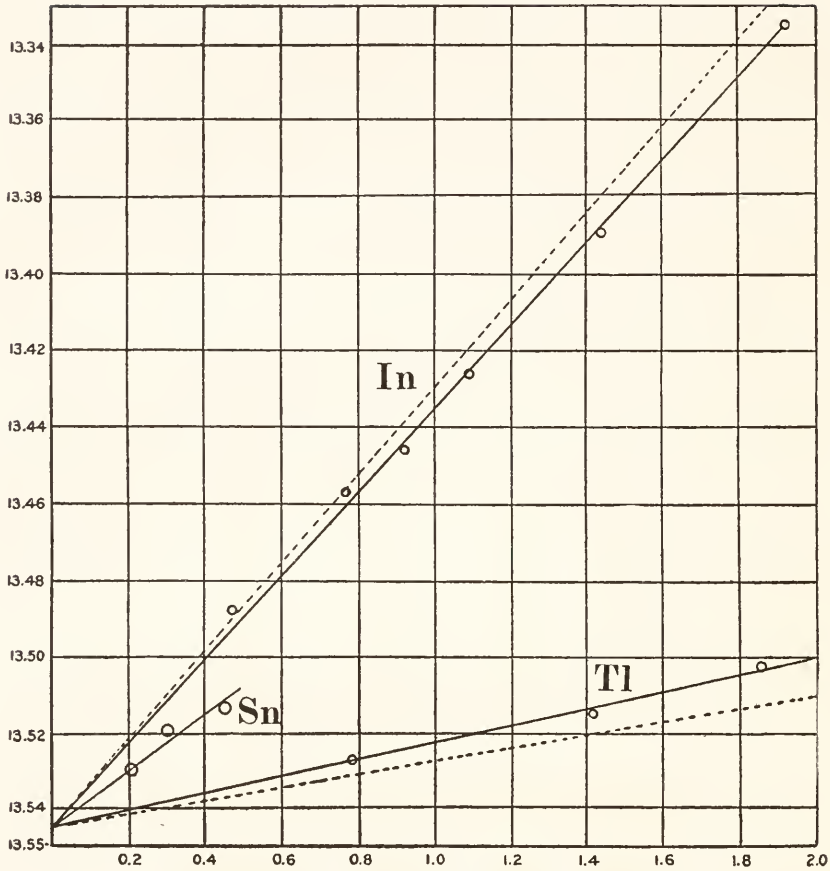

Fig. 3. Densities of Thallium, Indium, and Tin Amalgams.

Densities are plotted as ordinates, per cents by weight of solute in amalgam as abscissæ. The continuous lines represent actual densities, the dotted lines the averaged densities of the components, that is, the density which the amalgam would have possessed if there had been no change of volume on mixing. The dotted line for tin coincides essentially with that for indium.

THE CELL.

The multiple cell used in all the measurements of electromotive force is shown in fig. 4. This apparatus, devised by Richards and Forbes, must be very carefully annealed, for even at the best the glass receptacle is very fragile. The body of the vessel is used to hold the electrolyte; the four cups contain the amalgams to be measured. The advantage of the four cups is obvious: six different measurements may be made at one filling, and at the same time important checks can be secured on the accuracy of the readings.

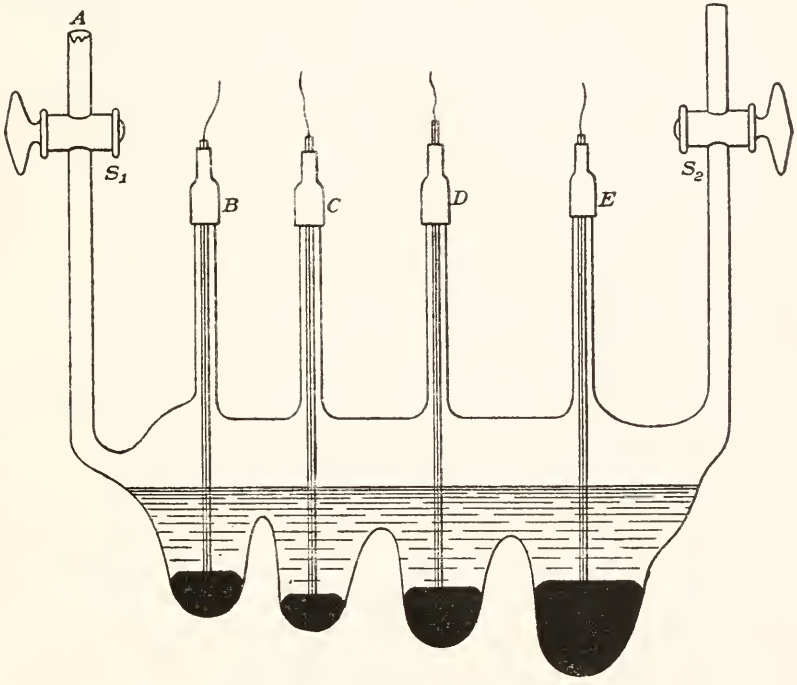

Fig. 4. Amalgams in Cell ready for Potential Measurement.

The glass receptacle was carefully cleaned and dried, and fused at A to the delivery tube of an apparatus supplying pure hydrogen. A vacuum pump was now attached at S_2 and the whole cell exhausted as far back as the stopcock S_1. The tops of the tubes, B, C, D, and E were closed with small pieces of rubber tubing and glass rod. When the pressure had been reduced to about 20 mm., the stopcock S_2 was closed and the cell allowed to fill with hydrogen through S_1. This was repeated four times. The glass rod was now removed from one of the tubes and the fine tip of a pipette, containing the proposed electrolyte, inserted. The issuing stream of hydrogen prevented the diffusion of air into the cell. When the vessel was about half full of the aqueous solution, the pipette was withdrawn and the stopper was replaced. In the same manner suitable amounts of the

various amalgams and mercury were introduced into the four cups. Finally, the electrodes, sealed into narrow glass tubes, were introduced—care being taken that the platinum points did not touch the glass. S_1 was now closed, the coil broken off from the hydrogen supply, and the vacuum connection removed from S_2. After gentle shaking for several minutes, the completed cell was transferred to the thermostat, and the measurements soon begun.

Amalgams prepared thus remained bright as long as was necessary and showed no signs of oxidation. It is evident that Hulett and De Lury did not fully read the somewhat similar description by Richards and Forbes, or they would not have suggested that the method contained faults which existed only in the preliminary work, not in the procedure finally adopted.[26]

The manner of adjusting the wires connecting the potentiometer to the cell should be mentioned. In the first trials long platinum wires dipping in the various amalgams were connected with the copper wires by means of mercury cups. The junctions of unlike metals were thus outside of the thermostat—an objectionable feature. Accordingly, in the final measurements only a short length of platinum wire was fused in the bottom of each tube dipping into the cell, and above this was placed, inside the tube, a drop of mercury. The copper wires were now pushed down the narrow tubes until connection was made with this drop. The contact of unlike metals was now deep in the cell and, being at constant temperature, could cause no disturbance.

Most of the potentials were measured at 30° and 0°, and many of the thallium cells were also measured at 15°. The temperature of the 30° bath was kept constant by means of a sensitive electrical regulator. A large heating coil was used in place of an incandescent lamp as the source of heat, since it avoids any disturbing effect due to radiant energy when the heater is in frequent operation. The temperature of this bath was always constant within 0.01°. The 15° bath was exactly similar except that it was equipped with a cold-water coil in order to compensate for the higher temperatures of the surroundings. For the zero bath a metal trough was filled with clean, finely crushed ice, covered with distilled water. This trough was placed in a larger one, the space between being filled with ice, and the box in turn was tightly packed in sawdust. This arrangement gave a very constant temperature. The temperatures of all the thermostats were determined with small Beckmann thermometers, capable of being read to within 0.005°; they were standardized by comparison with a very accurate Reichsanstalt thermometer, taking all the precautions necessary for ascertaining the temperature to within 0.01°.

[26] Compare Hulett and De Lury, Journ. Am. Chem. Soc., **30**, 1809 (1908) with Richards and Forbes, Publication of Carnegie Institution of Washington, No. 56, page 40 (1906).

THE POTENTIOMETER.

Considerable time was spent in the elaboration of a suitable potentiometer for use in this work. The arrangement used by Richards and Forbes, while probably accurate to 0.000005 of a volt, was complicated and involved troublesome calibrations. Moreover, it seemed desirable to dispense with the one-volt element and compare the drop of potential directly with a standard Weston cell. The arrangement finally adopted is shown in fig. 5. It was elaborated with the help of R. N. Garrod-Thomas, and was used also for his work, to be described later.

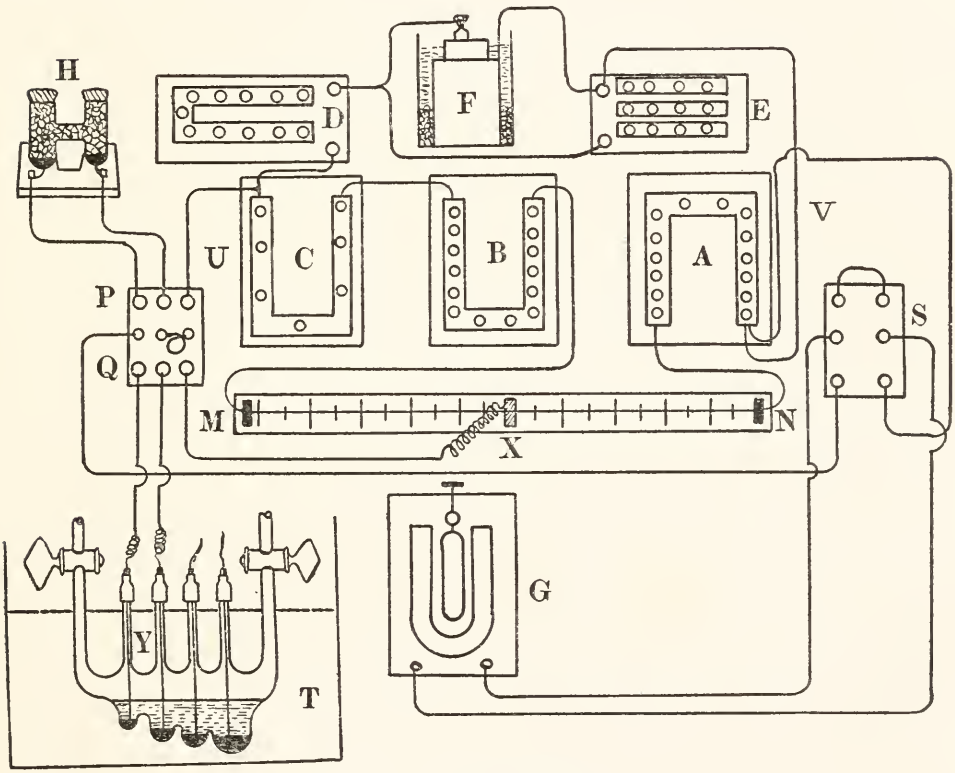

Fig. 5. The Potentiometer.

A large Daniel cell *F* was used as the source of the fall of potential. When in use, it was found best to keep it short-circuited through a resistance of about 300 ohms in the box *E*. The rough box *D* was so adjusted that the fall of potential between the points *U* and *V* was equal to 1.0184 volts, as measured against the normal cell *H*. *C* was a constant resistance of 9000 ohms. *A* and *B* were resistance boxes of 1111 ohms each, and *MN* was a manganin wire of 1.063 ohms resistance. At the commence-

ment of a measurement, the plugs were all placed in the box A and all removed from B. The resistance between U and V under these conditions was 10,112.06 ohms, embracing a drop of potential of 1.0184 volts, as given above. By removing plugs from A to the corresponding place in B, in order to keep the drop of potential constant, and manipulating the slider X, it was easy to compensate the potential of the unknown cell by opposing potential tapped from the box A and the slide-wire bridge, since the potentials measured never amounted to as much as 0.1 volt.

Suppose the total reading of the box A and the slide wire to be a ohms. Then the potential of the cell measured would be $\frac{a}{10,112.06} \times 1.0184$ volts. The factor $\frac{1.0184}{10,112.06}$ being a constant value, its logarithm was found once for all, and entered into all calculations.

In following this mode of procedure, the only portion of the resistance which needs very accurate calibration is the box A. The wire MN was 65 cm. in length, and was divided by a scale into divisions 6.10 mm. long, each of these corresponding to the millionth of a volt. Since the total fall of potential in the wire was only about 0.0001 volt and preliminary calibration showed it to be very uniform in resistance, no correction was deemed necessary for the readings of this scale under the wire. PQ was a three-way switch. When thrown towards P, the standard cell H was balanced against the fall of potential between U and V. When thrown toward Q, the potential was ready to be balanced against a portion of the bridge MN and box A. The galvanometer G of the d'Arsonval variety was manufactured by the Leeds and Northrup Company, of Philadelphia, and is designated by them as Type H. It was read with a telescope and scale at a distance of 60 cm. S was a double-rocker switch, the base of which was a thick plate of ebonite. It was so arranged that the galvanometer was either in the circuit or short-circuited itself. The galvanometer was extremely sensitive, and when short-circuited it returned to zero without any oscillations whatever. The whole potentiometer with the exception of the galvanometer was placed inside of a large glass case with a swinging door in order to avoid disturbing effects from changes of temperature and impurities in the atmosphere.

The apparatus, as described above, was used in the measurements on thallium amalgam cells and was easily accurate to within three or four millionths of a volt. Since thallium under the conditions of the measurements was univalent, and consequently gave comparatively large potentials, the above accuracy was fully sufficient; but in the case of trivalent indium, which for equal concentrations gives potentials only one-third as large as those of a univalent metal, even greater accuracy was desirable.

As has been previously mentioned, the portion of the bridge wire *MN* corresponding to one ohm was divided into 100 parts, giving direct readings to 0.000001 volt for each 6 mm. of wire. The graduation of the instrument was therefore adequate; improvement was to be attained only by eliminating all irregularities; and prominent among these, as every one knows, are thermoelectric effects due to junctions of dissimilar metals.

Two ways of suppressing thermoelectric effects are available: one, to use only one metal; the other, to keep the temperature the same throughout. The latter method was in the present case the more convenient. It was at first found that the temperature at the two ends of the glass case containing the potentiometer differed by as much as 0.5°. Part of this difference was traced to the proximity of an incandescent light, which was removed; but there still remained a considerable variation. This was finally overcome by the use of a small revolving fan which was attached to an axle run through one of the corners of the case and driven at high speed by a motor. Thus the air was stirred and kept at the same temperature throughout. Contact of the operator's hand with the bridge slide was obviated by the use of two cords attached to opposite sides of *X* and passed through small holes in the ends of the case; and the final adjustment was made on the bridge with the case closed. In this way another frequent source of irregularity was avoided and the readings were improved. The room in which all the apparatus was placed was kept as constant in temperature as possible.

In seeking for the causes of the yet remaining fluctuations, it was found that the galvanometer was influenced by the proximity of the observer, and even more so by heat-effects due to the operation of the rocker switch *S* with the hand. Therefore, the galvanometer was removed some distance from the apparatus and screwed against a very firm wall, the connections being made by insulated copper wires incased in glass tubes. The case of the galvanometer was packed in felt and covered with a sheath of copper, a small hole permitting a view of the mirror; and the instrument was read by a telescope and scale placed at a distance of about 130 cm. The rocker switch *S* was placed inside the case and operated from outside by means of a long cord, the observer being seated at the telescope some distance away.

The resistance box *A* was standardized by substitution. A sensitive Wheatstone bridge was used and the corrections on the various resistances were determined and tabulated exactly as if they were weights.[27]

Only two of the corrections thus found were as much as 0.01 ohm, and since each 0.01 ohm corresponds to very nearly 0.000001 volt, it is easily seen that all others were negligible. The two in error were the 300 and

[27] Richards, Proc. Am. Chem. Soc., **22**, 144 (1900).

400 ohm coils; and the deviation of these amounted to only 0.000002 and 0.000001 volt respectively. The boxes *B* and *C* were of the same quality as *A* and a preliminary standardization showed them to be fully as accurate. Since the resistances in *B* and *C* need be known only one-tenth as accurately as those in *A*, any corrections on these boxes would be supererogatory. The one important point, that 1000 ohms in *A* should be exactly one-ninth of the 9000 ohms in *B*, within 0.01 per cent, was demonstrated.

The standard Weston cells were made up from pure material as recommended by Hulett. These cells were compared with one another and also with three similar cells kindly loaned by Dr. H. L. Frevert. They all furnished the same value to within 0.0001 volt at 20°, and for their value the electromotive force 1.0184 was accordingly assumed.

The improved potentiometer described above appeared to be accurate to within a microvolt (0.000001 volt)—a high degree of precision.

ELECTROMOTIVE FORCE BETWEEN THALLIUM AMALGAMS.

With the apparatus and materials which have been described, measurements upon a variety of amalgams were executed. The description of a preliminary experiment will be given in detail, in order that the method may be more thoroughly understood. Amalgam I was prepared in the closed apparatus by depositing into 180.557 grams of mercury the amount of thallium equivalent to 0.9473 grams of silver (deposited in a coulometer in the same circuit), that is to say, 1.7915 grams of thallium, if silver and thallium are assumed to have the atomic weights of 107.88 and 204.03 respectively. Hence the amalgam contained 0.9822 per cent of thallium by weight.

One portion of this amalgam was introduced into one cup of the multiple cell, and another weighed portion was introduced out of contact with air into another cup, being diluted by the addition of a weighed amount of the pure mercury, which had been preserved in hydrogen as previously described. The second cup contained 36.513 grams of mercury, and received 25.721 grams of amalgam. It is easy to calculate that the dilute amalgam must have contained 0.4059 per cent of thallium. In order to mix thoroughly the amalgams and mercury in the second cup, the cell was gently shaken for some time, great care being taken to avoid any splashing from one cup to another. The cell was then introduced into the 30° thermostat and, after it had acquired the temperature of the bath the readings were begun. Two measurements of the cell gave values of 25.235 and 25.238 millivolts respectively, in mean 25.237.

The potential remained very constant over a considerable interval of time. Two entirely separate measurements taken with the same cell 48

hours later gave the values 25.231 and 25.243, in mean 25.237, exactly the same as before. In subsequent work the agreements were of this order of accuracy; usually average values alone will be given.

It is worthy of remark in this connection that the electrolyte was not found to be the least alkaline to phenolphthalein after thus standing for 48 hours over a thallium amalgam. This fact is very satisfactory, not only with regard to thallium, but also in its implication concerning the probable integrity of amalgams of less easily oxidized metals, whose oxides are less easily detected.

It is interesting to compare the result with the ideal value calculated from the gas law. The theoretical potential, calculated according to the formula

$$\pi = \frac{8.316 \times (273.09^\circ) \times 2.3026}{96{,}530} \log \frac{c_m}{c_n}$$

is 23.064 millivolts. This is 2.183 millivolts, or nearly 10 per cent, less than the observed value 25.237.

Having thus cleared the way by this preliminary work, four series of more accurate measurements were made. Four multiple cells containing thallium amalgam, designated A, B, C, and D, were prepared. In each case an amalgam prepared electrolytically was placed in cup 1; and cups 2, 3, and 4 were filled with the same amalgam diluted (in an atmosphere of hydrogen) with weighed amounts of mercury.

The "parent amalgam" in cups A1 and B1 was made by depositing in 197.33 grams of mercury the amount of thallium equivalent to 0.4290 gram of silver. This amalgam was diluted as follows:

grams of amalgam.	grams of mercury.	
13.272	+ 82.933	in A2
15.679	41.938	A3
23.710	32.791	B2
6.838	97.483	B3
11.736	83.642	B4

The "parent amalgam" in cup C1 was made by depositing in 168.361 grams of mercury the amount of thallium equivalent to 1.6738 grams of silver. This amalgam was diluted as follows:

grams of amalgam.	grams of mercury.	
12.487	+ 31.420	in C2
10.710	75.495	C3
10.448	112.095	C4

Finally the "parent amalgam" in cup D1 was made by depositing in 213.65 grams of mercury the amount of thallium equivalent to 0.2289 grams of silver. This amalgam was diluted as follows:

grams of amalgam.	grams of mercury.	
14.967	+ 29.589	in D2
8.851	75.453	D3
9.461	122.984	D4

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The electrical measurements made with these amalgams are summarized in table 2, together with the theoretical values calculated upon the assumption that the gas law applies with exactness, according to the concentration equation:

$$\pi = \frac{RT}{F} ln \frac{c_m}{c_n}$$

TABLE 2.—*Electrical Measurements of Thallium Amalgams.*

Designation of cup containing amalgam.	Approximate per cent of thallium in amalgams.	Exact value of $\log \frac{c_m}{c_n}$	Electromotive force between each pair of cups, in millivolts.					
			0°C.		15°C.		30°C.	
			Observed.	Theoretical.	Observed.	Theoretical.	Observed.	Theoretical.
A1	0.410							
		0.56502	31.543	30.608	33.166	32.290	34.810	33.971
A2	0.111							
		0.29498	16.360	15.980	17.238	16.858	18.110	17.735
A3	0.0565							
B1	0.410							
		0.37694	.....	.....	.....	.....	23.523	22.664
B2	0.172							
		0.53272	.....	.....	.....	.....	32.408	32.026
B3	0.0512							
		0.27338	.....	.....	.....	.....	16.531	16.436
B4	0.0269							
C1	1.8456							
		0.54518	33.897	29.533	35.511	31.155	37.134	32.775
C2	0.5249							
		0.35943	20.485	19.471	21.530	20.541	22.610	21.610
C3	0.2294							
		0.16340	9.118	8.852	9.601	9.338	10.090	9.824
C4	0.1575							
D1	0.220							
		0.47203	.....	.....	.....	.....	28.964	28.379
D2	0.074							
		0.50556	.....	.....	.....	.....	30.592	30.455
D3	0.0231							
		0.16729	.....	.....	.....	.....	10.114	10.058
D4	0.0157							

The measurements with cell B at the lower temperatures were unsatisfactory, and were rejected; cell D was measured only at 30°.

Each observed figure is the mean of at least three measurements. For example, the D1–D2 was found to have a potential of 28.969 millivolts by direct measurement. D1–D3 was found to be 59.551, and D2–D3, 30.596. Subtracting, we find again D1–D2 = 28.955. In the same way, by subtracting the observed value for D2–D4 from that for D1–D4, the value 28.969 is found. The mean value 28.964 is given; the same practice was adopted in all cases.

The difference between the observed and the ideal values is usually great; in the case of the concentrated cell, C1–C2, it amounts to 13 per cent. Further study of the figures shows that as the dilution is increased, this difference between the observed and calculated potentials diminishes, becoming only about 0.6 per cent in the case of the very dilute cell D3–D4. Deviations from the theoretical are always positive; the cell always gives a potential higher than the value computed simply from its concentrations. Cells of thallium amalgams thus appear to behave in a fashion similar to those of cadmium with increasing dilution, although in the case of the thallium cells the deviations are larger. Zinc varies in the opposite direction.

The results of these measurements and calculations are plotted graphically below according to the method employed by Richards and Forbes, which affords a convenient method of noting the departure of the cells from the gas law. In fig. 6 there are plotted as abscissæ the logarithms of the volumes occupied by a given weight of amalgamated thallium, taking the volume of the most concentrated amalgam in cup C1 as unity. The progress of the curve in the direction of ordinates between the points corresponding to any two volumes indicates the extent of the deviation from the theory of the electromotive force of the cell made from the two indicated amalgams. The curve is built up by plotting first the results with cell C, then those with cells A and B, and finally those with cell D. In each case as the drawing progressed the "parent amalgam" was started at its proper concentration on the curve already drawn; and this proceeding of necessity fixed the other points obtained from that particular cell. If into each cell a two-phase amalgam, having a constant potential, had been introduced, according to the excellent suggestion of Hulett and De Lury, the construction of this curve would have been somewhat facilitated; but the final result would have been identical. In this case greater care about perfect constancy of temperature would have been necessary. The regularity of the curve affords strong evidence of the accuracy of the measurements.

The curve for the thallium amalgams, like those for both zinc and cadmium, shows that as dilution is increased the potential of any cell approaches nearer and nearer to the requirement of the simple concentration law; that is to say, the slant of the curve becomes less and less. Complete horizontality would indicate complete fulfilment of the gas law. The regular form of the curve indicates the absence of oxidation in the more dilute amalgams, one of the most insidious sources of error in this sort of work. Thallium amalgams are extremely sensitive to oxidation and its elimination in these measurements is a source of gratification.

The results depicted by this curve will be discussed later in connection with the results for the other metals.

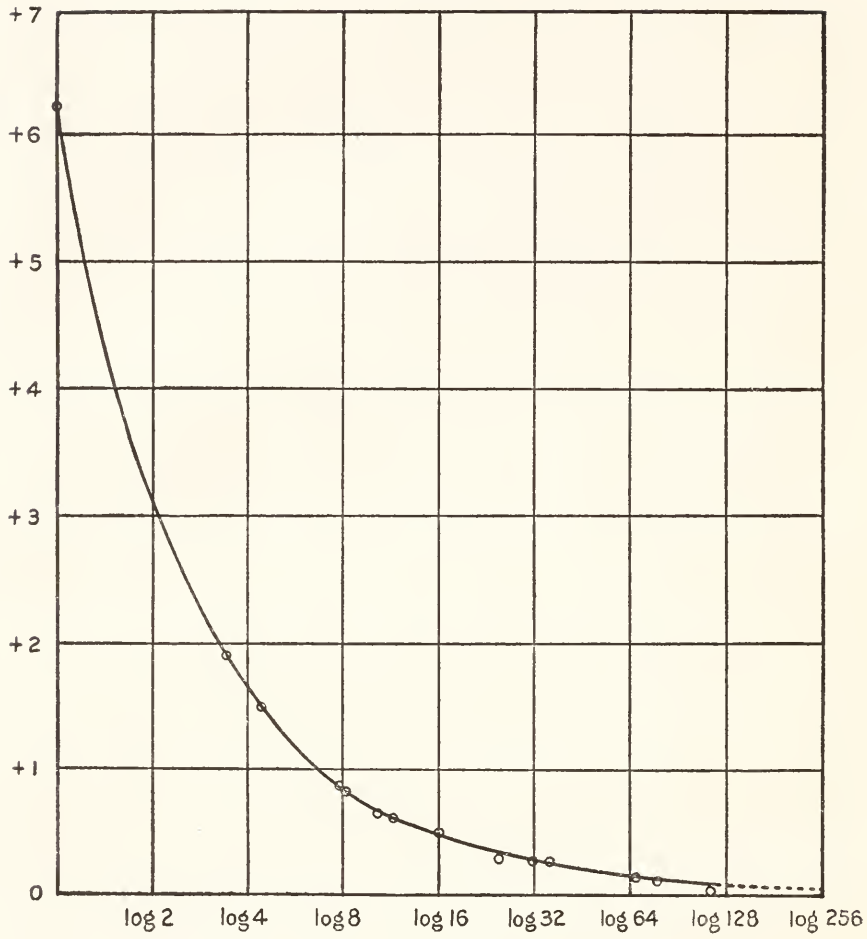

Fig. 6. The Deviations of the Electromotive Force of Thallium Amalgams.

Deviations from the expression $\pi = \frac{RT}{F} ln \frac{c_1}{c_2}$ are plotted in millivolts as ordinates, the logarithms of the concentration ratios as abscissæ. The most concentrated amalgam contained 1.85 per cent by weight of thallium and 98.15 per cent by weight of mercury. A horizontal line on the diagram would indicate complete fulfilment of the concentration law. This curve is almost if not quite independent of temperature, at least between 0° and 30°.

ELECTROMOTIVE FORCE BETWEEN INDIUM AMALGAMS.

Amalgams of indium were now studied in the same manner. They had been prepared in the fashion described on page 9, and all the dilutions were made inside the cell in an atmosphere of hydrogen with the same precautions as in the case of thallium. Density corrections were applied in the calculation of the concentration ratio.

Three parent amalgams, E1, F1, and G1, were prepared. The first, E1, contained 3.0014 grams of indium dissolved in 152.783 grams of mercury; the second, F1, 23.276 grams of this amalgam with 116.472 grams more of mercury, and the third, G1, contained 40.812 grams of F1 with 72.926 grams more of mercury.

These "parent" amalgams were diluted as follows:

grams of amalgam.		grams of mercury.			grams of amalgam.		grams of mercury.		
10.368	E1	+ 41.883	in	E2	8.498	F1	+ 71.897	in	F3
9.732	E1	+ 68.490		E3	8.543	F1	+ 118.680		F4
8.074	E1	+ 123.133		E4	8.177	G1	+ 58.144		G2
11.727	F1	+ 36.564		F2	9.328	G1	+ 102.808		G3

The measurements of electromotive force, and the theoretical values calculated from the concentration law, are given in table 3.

TABLE 3.—*Electrical Measurements of Indium Amalgams.*

Designation of cup containing amalgam.	Approximate per cent of indium in amalgams.	Exact value of $\log \frac{C_m}{C_n}$	Electromotive force between each pair of cups, in millivolts.					
			0°C.			30°C.		
			Observed.	Theoretical.	Difference.	Observed.	Theoretical.	Difference.
E1	1.92							
		0.69705	14.455	12.587	1.868	15.786	13.967	1.819
E2	0.384							
		0.20111	3.823	3.631	0.192	4.231	4.030	0.201
E3	0.242							
		0.30466	5.692	5.501	0.191	6.287	6.106	0.181
E4	0.120							
F1	0.319							
		0.61381	11.387	11.083	0.304	12.616	12.301	0.315
F2	0.078							
		0.36079	6.588	6.515	0.073	7.311	7.231	0.080
F3	0.034							
		0.19750	3.666?	3.566	0.100?	3.989	3.958	0.031
F4	0.021							
G1	0.016							
		0.31887	5.775	5.758	0.017	6.411	6.390	0.021
G2	0.008							
		0.16941	3.035	3.003	0.032	3.430	3.390	0.040
G3	0.00							

Comparison of the observed and calculated potentials of the indium amalgam cells shows the behavior of these cells to be similar to those of thallium, but in a less degree. The cells with concentrated amalgams show considerable deviation from the theoretical value, not so much, however, as with thallium amalgams of the same concentration. On the other hand, at great dilutions the agreement between the observed and calculated values is exceedingly close. The cell G1–G2 differs by only 0.000019 volt or 0.3 per cent from the theoretical potential.

The significance of the results of these measurements can best be illustrated by the same sort of curve as was employed in the case of thallium amalgams. The curve for indium amalgams is shown in fig. 7. As before, the common logarithms of the concentration ratios are plotted as abscissæ and the value of the deviations from the simple concentration law as ordinates. The sign of curvature is the same as with thallium, since both deviate in the same direction from theory.

The significance of this curve also will be discussed later.

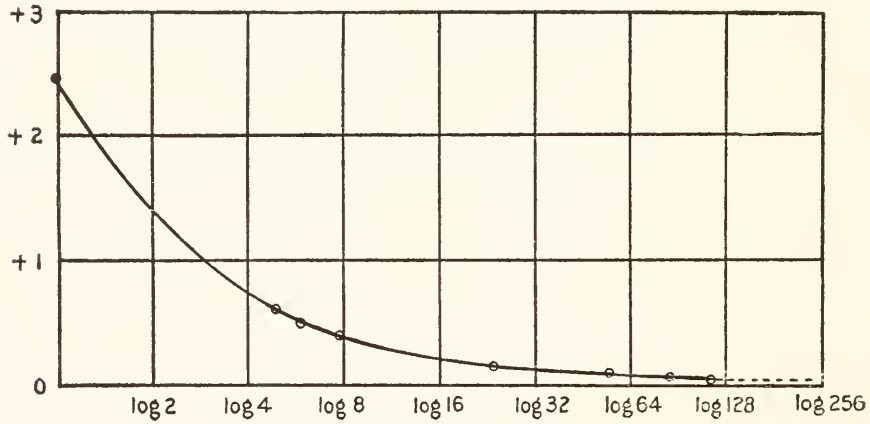

Fig. 7. The Deviations of the Electromotive Force of Indium Amalgams.

Deviations from the expression $\pi = \frac{RT}{3F} ln \frac{c_1}{c_2}$ are plotted in millivolts as ordinates, the logarithms of the concentration ratios as abscissæ. The most concentrated amalgam contained 1.92 per cent by weight of indium and 98.08 per cent by weight of mercury. A horizontal line on the diagram would indicate complete fulfilment of the concentration law. This curve is almost if not quite independent of temperature, at least between 0° and 30°.

ELECTROMOTIVE FORCE BETWEEN TIN AMALGAMS.

The tin amalgams were prepared in a manner similar to that employed with indium. The electrolyte used in the cells was a solution of stannous chloride, about half normal. Before use it was allowed to stand over pure tin and was then preserved under hydrogen. Great care was taken to insure the absence of stannic compounds.

Since concentrated tin amalgams deposit a solid phase on cooling to 0°, the first series of measurements were performed by the dilution of an amalgam containing 0.66 per cent by weight of tin—less than half of the higher concentration used by Cady. As even this was found to separate a solid at 0°, another series was made beginning with an amalgam containing only 0.21 per cent of tin.

The data concerning the preparation and dilution of these amalgams were as follows: 1.0766 grams of metallic tin were dissolved in 161.161 grams of mercury to make amalgam H1. This was diluted as follows:

grams of amalgam.	grams of mercury.	
17.351	+ 39.593	in H2
13.279	+ 99.824	H3
10.391	+ 147.265	H4

The more diluted series was made from a "parent" amalgam obtained by dissolving 0.3116 grams of tin in 149.021 grams of mercury. From this were prepared:

grams of amalgam.	grams of mercury.	
18.537	+ 44.845	in J2
16.436	+ 113.312	J3
9.919	+ 117.947	J4

TABLE 4.—*Electrical Measurement of Tin Amalgams.*

Designation of cup containing amalgam.	Approximate per cent of tin in amalgams.	Exact value of $\log \frac{C_m}{C_n}$	Electromotive force between each pair of cups, in millivolts.					
			0°C.			30°C.		
			Observed.	Theoretical.	Difference.	Observed.	Theoretical.	Difference.
H1....	0.66	0.51495	7.632	13.949	−6.317	13.182	15.480	−2.298
H2....	0.20	0.41401	10.614	11.213	−0.599	11.820	12.447	−0.627
H3....	0.077							
J1.....	0.210	0.53655	13.612	14.532	−0.920	15.156	16.128	−0.972
J2.....	0.061	0.36025	9.548	9.758	−0.210	10.622	10.829	−0.207
J3.....	0.027	0.21345	5.715	5.781	−0.066	6.371	6.416	−0.045
J4.....	0.016							

Examination of these results shows that the observed potentials of the amalgam cells of tin, like those of all the other metals thus far studied, approach the theoretical requirements more and more closely as the dilution is increased. The results are depicted graphically by the curve in fig. 8. It should be noted that the sign of curvature is exactly the reverse of that of the otherwise similar curves obtained with cadmium, thallium, and indium amalgams, since tin amalgams deviate in the opposite direction from theory. In this respect tin is similar to zinc.

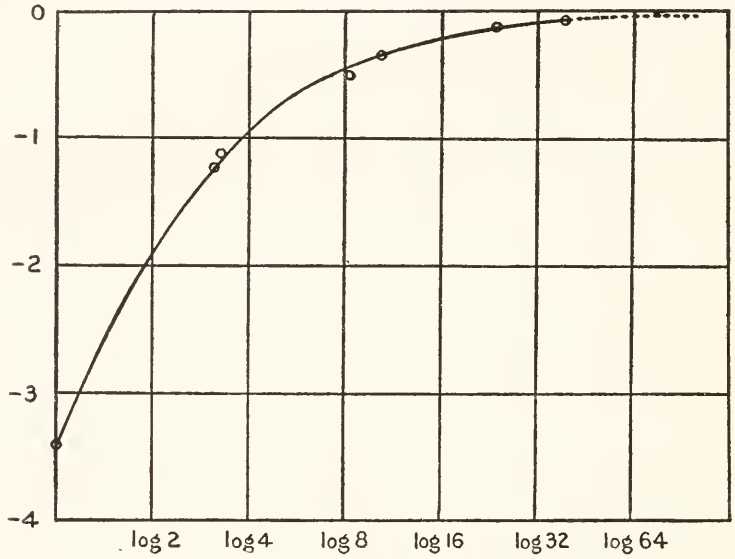

Fig. 8. The Deviations of the Electromotive Force of Tin Amalgams.

Deviations from the expression $\pi = \frac{RT}{2F} ln \frac{c_1}{c_2}$ are plotted in millivolts as ordinates, the logarithms of the concentration ratios as abscissæ. The most concentrated amalgam contained 0.66 per cent by weight of tin and 99.34 per cent by weight of mercury. A horizontal line on the diagram would indicate complete fulfilment of the concentration law. This curve is for 30°. The most concentrated amalgam separates solid at 0°.

In the case of the tin amalgam cells complete exclusion of oxygen is necessary, not only on account of the amalgams, but also in order to insure the stability of the electrolyte, since stannous chloride when exposed to the air quickly becomes basic according to the equation:

$$3SnCl_2 + \tfrac{1}{2}\ O_2 + H_2O = 2SnClOH + SnCl_4$$

When the solution is in contact with tin amalgam in the air this reaction proceeds very rapidly, perhaps because the stannic chloride is reduced by the amalgam. The formation of stannic chloride would be expected to lower the potential, and the constancy observed in the values of the various cells proves the complete elimination of any such disturbing effect.

With the idea of testing the effect of stannic chloride, but without much hope of obtaining results fully corresponding to a quadrivalent ion, a further attempt was made to measure a tin amalgam concentration cell, using an electrolyte containing at first pure stannic chloride. Pure tin was dissolved in aqua regia and the nitric acid was removed by boiling repeatedly with fresh portions of hydrochloric acid. The solution was then diluted with water, most of the free acid was neutralized with sodium hydroxide, and the solution containing all its tin in the state of highest oxidation was placed in the cell.

No constant readings could be obtained with any of the tin amalgams under these conditions. Evidence was obtained, however, that this electrolyte tended to give lower potentials than those obtained with stannous chloride. For example, with a cell whose calculated potential would be 0.01605, if the tin were quadrivalent, and 0.0321, if bivalent, a value of 0.0262 was obtained. Clearly, as we had expected, ionized quadrivalent tin is not in a state of electrochemical equilibrium with tin amalgam.

Cady[28] supposed that he attained this equilibrium by using potassium stannate as an electrolyte, but in our opinion it is extremely doubtful if in a solution of a stannate, the quadrivalent tin ion is in reversible equilibrium with a tin amalgam. Our practical experience confirms this conclusion. We attempted to measure a cell with a solution of sodium stannate as its electrolyte, but were unable to obtain anything approaching constant potentials.

We regret to state that another fact also points to the conclusion that Cady's work with tin was questionable. Roozeboom and van Heteren have shown that at 25° tin amalgams containing from 1.2 to 99 "atom per cent" of tin give the same potential, there being present two phases of invariable composition—a liquid phase containing 1.2 "atom per cent" tin and a solid phase of 99 per cent tin. But Cady supposed he had made a tin amalgam of 1.73 per cent by weight or nearly 3 atom per cent, when he used potassium stannate as electrolyte in the attempt to obtain the potential of a cell in which tin behaved as quadrivalent. He calculated the concentration ratio on the basis of his supposed percentage.[29] In the light of the work of Roozeboom and Van Heteren this work is evidently faulty, since the strongest liquid amalgam in the cell could not have exceeded 0.8 per cent by weight of tin, and the more dilute amalgam might have been affected by crystals of tin dissolved on dilution. Clearly Cady's work on tin is without significance.

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[28] Jour. Phys. Chem., **2**, 551 (1898). Attention should be called to another serious error in Cady's paper, of which due acknowledgment was made. (Ibid., 3, 107 [1899]). All this work of Cady's was done under the direction of W. D. Bancroft.

[29] Professor Cady has kindly looked up his data in his original note-books, and finds that the mistake was not an error of proof-reading, but arose from lack of knowledge of the solubility of tin in mercury.

THE TEMPERATURE COEFFICIENT OF THE AMALGAM CELLS.

Since all the potentials have been measured at two or three tempera tures, interest next centers in the computation of the temperature coefficients of the various cells. The temperature coefficient $\frac{\Delta\pi}{\Delta T}$ over a finite range of temperature is conveniently divided by the potential at 0°, in order to compare the values obtained from the various amalgams with the same range.

The values of the quantity thus obtained, $\frac{\Delta\pi}{\pi_0 \Delta T}$, for the thallium, indium, and tin amalgams are given in the following table as calculated from the electromotive forces already recorded. The change of electromotive force between 0° and 15° was almost always essentially identical with that between 15° and 30°. On account of the comparatively small change of electromotive force, 15° is rather a small range for this purpose; therefore the whole range of 30° is given below as the basis for computing the temperature coefficient.

The values given in table 5 are arranged in the order of the concentration of the most concentrated amalgam in each cell. Thus the effect of concentration upon the temperature coefficient is to be ascertained at a glance.

TABLE 5.—*Temperature Coefficients of Electromotive Force.*

Thallium amalgams.			Indium amalgams.			Tin amalgams.		
Designation of cell.	Per cent of thallium of most concentrated amalgam in each cell.	$\frac{\Delta\pi}{\pi_0 \Delta T}$ 0° to 30°C.	Designation of cell.	Per cent of indium in the more concentrated amalgam in each cell.	$\frac{\Delta\pi}{\pi_0 \Delta T}$ 0° to 30°C.	Designation of cell.	Per cent of tin in the more concentrated amalgam in each cell.	$\frac{\Delta\pi}{\pi_0 \Delta T}$ 0° to 30°C.
C1–C2	1.85	0.00319	E1–E2	1.92	0.00309	J1–J2	0.21	0.00378
C2–C3	0.52	0.00350	E2–E4*	0.38	0.00350	H2–H3	0.20	0.00380
A1–A2	0.41	0.00346	F1–F2	0.32	0.00360	J2–J4	0.06	0.00378
C3–C4	0.23	0.00355	F2–F4*	0.08	0.00354			
A2–A3	0.11	0.00357	G1–G2	0.015	0.00364			

* The cells E2–E3 and F2–F3 had such small electromotive forces that the accurate measurement of the temperature coefficients was beyond the range of the apparatus. Therefore those cells were combined with cells E3–E4 and F3–F4 respectively, for the present purpose. It should be pointed out that the error involved in calculating the temperature of the indium cells is rather large, since the potentials are small, the metal being trivalent.

Although these results are not perfectly regular, and show evidence of experimental imperfection, their general tendency is clear.

The temperature coefficients of the thallium and indium amalgams exhibit very similar behavior. The concentrated amalgams give a value much lower than 0.00366 (the coefficient of expansion of the unit volume of perfect gas), but as the dilution is increased, the coefficient approaches nearer and nearer to the ideal value. The most dilute indium cell measured gave a value 0.00364, very nearly the theoretical coefficient. This same cell gave a potential only 0.4 per cent different from that demanded by the formula of von Türin; thus, as the electromotive force approaches the requirement of the gas law, the temperature coefficient does likewise.

APPLICATION OF THE EQUATION OF CADY.

The equation of Cady claims that the deviations from the simple equation of von Türin are due to the heat of dilution of the amalgams.[30] On comparing this equation

$$\pi = \frac{U}{\nu F} + \frac{RT}{\nu F} ln \frac{c_m}{c_n} \tag{3}$$

with the equation of Helmholtz

$$\pi = \frac{U}{\nu F} + T \frac{d\pi}{dT} \tag{1}$$

it is apparent that if the former really held true, the last terms of the equations would be identical. This was pointed out by Cady.

Placing the second members equal to one another and dividing through by T we obtain the expression

$$\frac{R}{\nu F} ln \frac{c_m}{c_n} = \frac{d\pi}{dT} \tag{4}$$

That is to say, the temperature coefficient should depend upon the relation of the concentrations, not upon the electromotive force which they happen to exert.

This consequence is readily tested by the data in hand. Take for example the cell C1–C2. Here $\frac{c_m}{c_n} = 3.516$, and its natural logarithm is 1.2574. Hence the first member of the above equation (4) becomes

$$\frac{8.316 \times 1.2574}{1 \times 96{,}530} = 0.0001082$$

and the second member becomes

$$\frac{0.037134 - 0.033887}{30.0^\circ} = 0.0001081$$

The agreement is so striking that other cases should be studied.

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[30] Journ. phys. Chem., **2**, 551 (1898).

Take for example B2–B3. Here $\frac{c_m}{c_n} = 3.4104$, and its natural logarithm is 1.2268. Hence the first member of the equation becomes

$$\frac{8.316 \times 1.2268}{1 \times 96{,}530} = 0.0001057$$

and the second member becomes

$$\frac{0.032408 - 0.029303}{30.0^\circ} = 0.0001035$$

Here the agreement is not so good; but, on the other hand, it might be worse. Another thallium amalgam cell, A1–A3, taken at random, shows essentially the same relation, the terms being as follows:

$$\frac{8.316 \times 1.9808}{96{,}530} = 0.0001700 \qquad \frac{52.920 - 47.903}{30.0^\circ} = 0.0001670$$

In the case of indium, a somewhat less percentage accuracy in fulfilling the requirements of the Cady equation is shown. For the cell E1–E2 the terms are these:

$$\frac{8.316 \times 1.6082}{3 \times 96{,}530} = 0.0000461 \qquad \frac{15.786 - 14.455}{30.0^\circ} = 0.0000444$$

With tin, about the same order of agreement is to be found. For example, in the cell, J1–J2, the first member of equation (4) becomes

$$\frac{8.316 \times 1.2365}{2 \times 96{,}580} = 0.0000532$$

and the second member becomes

$$\frac{15.156 - 13.612}{30.0^\circ} = 0.0000515$$

a difference of about 3 per cent, or about like that found in the case of indium.

One conclusion drawn from these partial agreements is the same as that drawn from the case of cadmium studied by Richards and Forbes, namely, that the equation of Cady does not contain an exact representation of all the influences producing electromotive force. On the other hand, the new results strongly reinforce the hope expressed in the earlier paper that this equation, although not wholly exact, is really a step in the right direction. For it is inconceivable that all these cells, possessing very different temperature coefficients, one as much as 13 per cent different from the requirement of the gas law, should all come within 3 per cent of the fulfilment of equation (4), if the equation were without meaning.

Expressed in other words, the meaning of the results and mathematical considerations just detailed may be stated as follows: *The reason for the deviation of the actual electromotive forces of amalgam cells from the values calculated from the concentrations is found to be primarily in the free energy of the change of chemical affinity involved in the dilution of*

the amalgams. The electromotive force may be looked upon as being due to at least two entirely different phenomena superposed: one, the "chemical free energy," which manifests itself as heat on dilution, and the other the "osmotic energy," due to the difference of concentration of the two different amalgams. In these cells all the free energy of the essentially chemical part of the change may be supposed to appear as heat, because the heat capacity of the system is essentially unchanged during the reaction; hence the system is peculiarly well adapted for tracing the mechanism of the chemical production of electromotive force.[31] This was indeed the reason why the whole investigation was undertaken. The probable reasons for the lack of exactness in the application of the equation of Cady will be discussed in the second half of the monograph, when other results have been presented.

APPLICATION OF THE EQUATION OF HELMHOLTZ.

The importance of the heat of dilution in the case of amalgam cells leads one to inquire concerning its exact values under the conditions of the present experiments. These values are most readily calculated from the well-known equation of Helmholtz, whose verity is undoubted. The only difficulty in the present case lies in the fact that the temperature coefficients were perforce determined over a rather large range of temperature—30°—on account of their otherwise too insignificant magnitudes. Moreover, even then their determination carries with it by far the largest percentage error of any part of the work. Fortunately the nearly if not quite linear nature of the coefficients with these metallic cells prevents the introduction of any considerable error from the large range needed.

In 1882, Helmholtz, in a paper already referred to, evolved the equation

$$\pi\nu F - U = \nu F T \frac{\Delta\pi}{\Delta T} \qquad (5)$$

an expression already given in a somewhat different arrangement as equation (1). According to this expression the sum of the heat of reaction and the product of the absolute temperature and the temperature coefficient of the change of free energy should equal the change of free energy itself.

The experimental work already described furnishes sufficient data for applying this equation to the amalgam cells of thallium, indium, and tin.

Take, for example, the thallium cell C1–C2. Here $\pi_0 = 0.033897$, $\Delta\pi = 0.003237$, $\Delta T = 30.00°$, $T = 273.09$, $\nu = 1$, and $F = 96{,}530$.

[31] Richards, Proc. Am. Acad., **38**, 293 (1902) "The relation of changing heat capacity to change of free energy, etc." This theorem has been recently expanded mathematically by Nernst, with the help of an interesting assumption concerning the extrapolation to the absolute zero.

Then

$$\pi_0 \nu F = \quad 3272.1 \text{ joules}$$
$$F \nu T \frac{\Delta\pi}{\Delta T} = \quad 2844.4 \text{ joules}$$
$$\text{Difference } U = + \quad 427.7 \text{ joules}$$

Thus upon the dilution with mercury of an amalgam containing nearly two per cent (1.846 per cent) by weight of thallium to about treble its volume (more exactly, 3.5 fold) we should obtain 428 joules or 102 small calories for every 204 grams of thallium.

Again, in cell C2–C3, $\pi_0 = 0.020485$, $\Delta\pi = 0.002125$, $\Delta T = 30.00°$, $T = 273.09$, $\nu = 1$, and $F = 96{,}530$. Then

$$\pi_0 \nu F = 1978 \text{ joules}$$
$$F \nu T \frac{\Delta\pi}{\Delta T} = 1869 \text{ joules}$$
$$\text{Difference } U = \quad 109 \text{ joules}$$

Turning now to the indium amalgams, we may consider for example the cell E1–E2, in which $\pi_0 = 0.014455$, $\Delta\pi = 0.001331$, $\Delta T = 30.00°$, $T = 273.09$, $\nu = 3$, $F = 96{,}530$.

Then

$$\pi \nu F = 4186 \text{ joules}$$
$$\nu F T \frac{\Delta\pi}{\Delta T} = 3509 \text{ joules}$$
$$\text{Difference } U = \quad 677$$

This difference, the heat of dilution, is here much larger even than in the concentrated thallium cell, because the electrochemical equivalent of indium is only about one-sixth as great as that of thallium. In the case of a cell with very dilute amalgams, on the other hand, the heat of dilution is almost negligible, as is shown by the following calculation of cell G1–G2, about a hundred times as dilute as the previous example. There

$$\pi \nu F = 1858 \text{ joules}$$
$$\nu F T \frac{\Delta\pi}{\Delta T} = 1862 \text{ joules}$$
$$\text{Difference } U = \quad -4 \text{ joules}$$

The agreement here is very satisfactory, being about 0.25 per cent. The minus sign can hardly be significant, as the probable error of the measurements is as great as 4 joules.

There now remains to be considered only the tin amalgam cells. For example, we have in one cell, H2–H3: $\pi_0 = 0.010614$, $\Delta\pi = 0.001206$, $\Delta T = 30.00°$, $T = 273.09°$, $\nu = 2$, $F = 96{,}530$. Then

$$\pi \nu F = 2284 \text{ joules}$$
$$\nu F T \frac{\Delta\pi}{\Delta T} = 2353 \text{ joules}$$
$$\text{Difference } U = -69 \text{ joules}$$

Thus the dilution of the tin amalgams gives a small *cooling* effect—a conclusion wholly in accord with the deviation of its potential from the equation of von Türin and Meyer. If more concentrated amalgam could have been used, the result would undoubtedly have been greater.

If possible, it would be well to verify these values of heats of dilution by actual experiment. Unfortunately, however, an accurate determination of the heat of dilution is only possible with the more concentrated amalgams, and even in these cases it is difficult. Five millionths of a volt in the potential of a concentration cell corresponds to the development of one joule during the transport of an univalent gram-atom. A mass of amalgam containing a gram-atom of thallium dissolved in 99 times its weight of mercury, when diluted with an equal volume of mercury would involve a heat capacity not far from 6000 mayers; hence one joule would produce a temperature change of less than 0.0002°. On account of the high inertia of mercury, the liquids do not mix easily; and for the same reason the plentiful stirring evolves much heat. The exact evaluation of the stirring correction is very difficult. Moreover, the dilution must be carried out in an indifferent gas in order to avoid oxidation with its attending heat effect.

Nevertheless, in spite of these difficulties the attempt was made to determine the heat of dilution in the cases of the more concentrated amalgams of thallium and indium. 1226 grams of a 1 per cent thallium amalgam were diluted with an equal bulk of mercury and found to cause a rise of 0.015° in a calorimetric system having a heat capacity of 431 mayers. On further diluting by an equal bulk of mercury the mixture resulting from this first experiment, the increased system (having now a heat capacity of 762 mayers) was raised through only 0.002°. These effects were in the expected direction, but not of the expected magnitude.

The experiments were conducted in the apparatus of Richards and Forbes, in which the mixing was conducted by a clock-work stirrer. Lack of time had prevented the proposers of this apparatus from testing it thoroughly. Our present experience indicates that the clock-work stirring was inadequate, and hence that an inadequate change of temperature must have been observed in all cases. Nevertheless, in spite of the quantitative inadequacy of these results, they are qualitatively of value; for they afford experimental evidence that the conclusions drawn from the equation of Helmholtz are at least in the right direction, and therefore that the data upon which the conclusions are based are not seriously in error.

In the case of indium, 150 grams of an amalgam containing 1.92 per cent of indium was diluted with 600 grams of mercury in a small calorimeter, the total heat capacity being 157 mayers. Here, in this smaller apparatus, the stirring was more effective, and the temperature rose 0.048°,

a result more nearly in accord with the expected value, but still below its full magnitude. The computation of the result is not worth while, as there can be no doubt that this experiment, like the others, has no more than qualitative value.

The small per cent of tin in a tin amalgam which remained wholly liquid at 0° corresponds to a heat of dilution which would cause a change of only 0.002° in the calorimeter—an amount too small to be determined within 50 per cent by means of our thermometers. Hence an attempt to carry out this experiment was without object.

In view of all these circumstances, we are inclined to agree with Carhart in thinking that the electrical method of determining the heats of dilution of amalgams is to be preferred to the thermochemical method.

It is worthy of note, in this connection, that the Helmholtz equation shows at once why the temperature coefficient of the electromotive force divided by the electromotive force approaches the coefficient of expansion of a perfect gas as the dilution of the amalgam proceeds. To illustrate this relation, the equation may be cast into a somewhat less familiar form. The normal form, transposed, is thus:

$$\nu F T \frac{\Delta\pi}{\Delta T} = \nu F \pi - U$$

Dividing through by $\nu F \pi T$, we obtain

$$\frac{\Delta\pi}{\pi \Delta T} = \frac{1}{T} - \frac{U}{\nu F \pi T}$$

Evidently, because U, the heat of dilution, diminishes as the dilution proceeds, the last term will become smaller and smaller. Finally, when the heat of dilution becomes negligible at great dilution, the equation will become simply $\frac{\Delta\pi}{\pi \Delta T} = \frac{1}{T}$.

Simultaneously, the equation of Cady

$$\pi = \frac{RT}{\nu F} ln \frac{c_m}{c_n} - \frac{U}{\nu F}$$

loses its last term, and becomes the simple concentration equation.

It is equally clear that a positive heat of dilution $(+U)$ will cause the potential to be high and the temperature coefficient to be low. In the case of thallium and indium, this was found actually to be the case. On the other hand, with a negative heat of dilution $(-U)$ the potential will be low and the temperature coefficient high. This was found to be the case with tin, and by Richards and Forbes with zinc.

Thus the theory of these cells seems to be complete, except for the quantitative understanding of the minor deviations from the equation of Cady. These deviations, which are probably to be traced primarily to the inaccuracy of the simple concentration ratio $\frac{c_m}{c_n}$ as an index of the precise

osmotic work to be obtained from the dilution of an amalgam, may best be discussed in the light of the further data presented in the next paper. Hence they will be deferred to the conclusion of the monograph.

In conclusion, it is a pleasure to express our indebtedness to the Carnegie Institution of Washington for the apparatus and materials used in this work.

SUMMARY.

The main points of the present research may be summarized as follows:

(1) The potentials between various liquid amalgams of thallium, indium, and tin were investigated at 30° and 0°. Many precautions were taken against experimental errors. The potentials of the thallium cells are thought to be reliable within 0.00001 volt; those of the indium and tin cells within 0.000005 volt.

(2) Thallium and indium amalgams gave potentials higher than those calculated from the simple concentration law; and tin amalgams gave potentials lower than those calculated from the simple concentration law.

(3) The temperature coefficients of the various cells have been calculated and found to approach the ideal value 0.00366 for a unit potential as infinite dilution is approached.

(4) The equation of Cady was applied to the results, and found to afford a fairly accurate explanation of the deviations from the concentration law in all three cases.

(5) The equation of Helmholtz was used for the calculation of the heats of dilution, and was found to account for the changes in the temperature coefficients.

(6) It was found impossible to obtain satisfactory results with an electrolyte containing tin in a quadrivalent condition, either as stannic chloride or as sodic stannate. In this connection it was pointed out that Cady must have had a two-phase amalgam in his tin cell, and that his results with tin were illusory.

(7) The density of pure indium was determined and found to be 7.28.

(8) The densities of various liquid amalgams of thallium, indium, and tin were carefully measured and compared with the calculated values.

SEPTEMBER 1907 TO JANUARY 1909.

II.

Electrochemical Investigation of Liquid Amalgams of Zinc, Cadmium, Lead, Copper, and Lithium.

By Theodore W. Richards and R. N. Garrod-Thomas.

INTRODUCTION.

Simultaneously with the work described in the foregoing paper a similar investigation upon other metals was begun in the laboratory. The parallel progress of these two investigations was an assistance to each, for not only were the potentiometer and other apparatus used in common, thus economizing time for each investigator, but also the experience gained in the one was immediately helpful in the other. The object of the work to be described was, of course, similar to that of the work just chronicled, namely, to extend as far as possible the study of liquid amalgams in their relation to thermodynamical theory and to the essential nature of solutions and the galvanic cell. The present paper contains, as its title indicates, an experimental study of the liquid amalgams of zinc, lead, copper, and lithium. It will be seen that the theoretical discussion of these results together with those concerning cadmium, thallium, indium, and tin, already described, furnishes much light upon these general questions and the outcome will be seen to have justified the time and trouble spent upon the somewhat exacting investigation.

ZINC AMALGAMS.

The energy changes involved in the dilution of zinc amalgams have recently been studied in this laboratory by Richards and Forbes.[32] Zinc amalgams of different concentrations, ranging from 0.9 per cent to about 0.015 per cent of zinc, were connected by means of an electrolyte consisting of zinc sulphate in water; and the potentials of the resulting concentration cells were measured, and were compared with the theoretical potential deduced from an equation derived from that of von Türin:[33]

$$\pi = \frac{RT}{\nu F} \ln \frac{c_1}{c_2}$$

[32] Carnegie Institution of Washington, Publication No. 56, p. 36 (1906).
[33] Zeit. phys. Chem., **5**, 340 (1890).

An attempt was made also to determine the heat which the amalgam of concentration c_1 would evolve or absorb on dilution to concentration c_2 in the case of one cell. In this trial a 0.9 per cent zinc amalgam on dilution by its own weight of mercury absorbed 52 joules per gram-atom of zinc.

It seemed very desirable that this thermochemical result should be verified by the application of the equation of Helmholtz:

$$\nu\pi F - U = \nu F T \frac{\Delta\pi}{\Delta T}$$

through the determination of the temperature coefficient of the electromotive force. Lack of time prevented this in the earlier work; accordingly the present investigation was undertaken.

The problem obviously involved simply the extension of the work of Richards and Forbes to two different temperatures, but the execution of the work was less easy than had been expected. Since the value of $\Delta\pi$ which would be expected in the case of the above cell is very small, it was found necessary to make ΔT somewhat large. Measurements were at first made at 30°, 15°, and 0°, but the interval of only 15° is too small to allow of an accurate measurement of the temperature coefficient, and so in the final experiments measurements were made at 30° and 0° C. only.

Most of this investigation was carried out in identically the same way as the earlier work, and the densities of the amalgams were taken from those results. The methods of purification of the zinc, zinc sulphate, and mercury, the methods of preparing the amalgams, of sealing them in hydrogen, and of introducing them into the cell, and diluting them with mercury, which had been distilled and sealed in hydrogen, were identically the same in every respect.

The potentiometer used was, however, considerably modified. If in a cell of a bivalent metal where $\frac{c_1}{c_2} = 2$, it is desired to distinguish between a temperature coefficient of 0.00366 and 0.00367, the potential of the cell at 30° and 0° must be measured with an error of not more than 0.000002 volt. Hence it was clear that a potentiometer more sensitive than that employed by Richards and Forbes would have to be used. Accordingly, much time was spent, with the help of J. Hunt Wilson, in elaborating a suitable potentiometer. As this instrument is described in detail in the foregoing paper,[34] any further account of it is unnecessary here.

The thermostats, also, were the same as those described there; they could be relied upon to keep at a temperature constant within 0.01°. The thermometers were accurately standardized by means of instruments bearing the certificate of the Reichsanstalt.

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[34] This monograph, pp. 17 to 20.

ELECTROMOTIVE FORCE BETWEEN ZINC AMALGAMS.

The first series of results with zinc amalgams, although not of sufficient accuracy to yield trustworthy temperature coefficients, are worth recording as a corroboration of the results obtained during the previous investigation of Richards and Forbes.

In the first case the most concentrated amalgam contained 0.90 per cent of zinc. It was placed undiluted in the first cup of the multiple cell described in the foregoing paper,[35] was diluted with mercury in the third and fourth cups, and finally the parent amalgam was again put undiluted in the remaining second cup, in order to be sure that no change had taken place in the amalgam during the filling of the cell, and also that the amalgam had been in the first place thoroughly mixed. This precaution was usually taken in the subsequent work also, but only in one case, mentioned later, was a difference greater than 0.000002 volt ever found between the first and the last portions of amalgam. As is shown below, the maximum difference in the present case was only one millionth of one volt.

In addition to this series of measurements, another was made upon three more dilute amalgams, in order to show the increasingly near approach of the potential to the gas law. Table 6 gives both series of measurements at 30°. The details of dilution, etc., need not be given as regards these preliminary results. The theoretical potential given below is calculated according to the simple concentration equation.

TABLE 6.—*Preliminary Electrical Measurement of Zinc Amalgams.*

Designation of cup containing amalgam.	Approximate per cent of zinc in amalgams.	Exact value of $\log \frac{C_m}{C_n}$	Electromotive force, in millivolts, between each pair of cups. 30°C.		
			Observed.	Theoretical.	Difference.
K1	0.900 } ..	0.0000	0.001	0.000	0.001
K2	0.900 } ..	0.37045	10.175	11.129	0.954
K3	0.384 } ..	0.21459	6.123	6.446	0.323
K4	0.234				
L1	0.100 } ..	0.44404	13.262	13.341	0.079
L2	0.036 } ..	0.26303	7.828	7.903	0.075
L3	0.020				

[35] This monograph, p. 15.

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These results confirm wholly the work of Richards and Forbes, carried out at 23°, showing that cells of zinc amalgams give a much lower electromotive force than that required by the concentration law. The quantitative agreement of the two series of results is shown in the accompanying diagram (fig. 9), where the points surrounded by single circles are the points found by the earlier work, and those surrounded by double circles the present data. This curve is drawn on the same scale as that used in the other similar curves in this monograph.

The cells were measured also at 15° and 0°. In no case did the potential between cups 1 and 2 exceed 0.000001 volt. At 30° the other measurements also were sufficiently concordant and convincing. At 0° the more dilute amalgams gave less consistent results, and evidently were not so

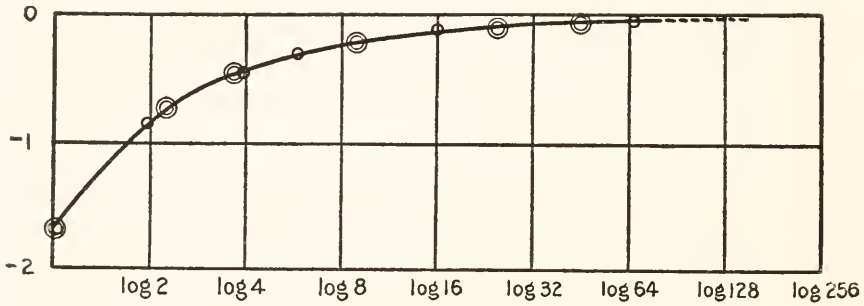

Fig. 9. The Deviations of the Electromotive Force of Zinc Amalgams.

Deviations from the expression $\pi = \frac{RT}{2F} ln \frac{c_1}{c_2}$ are plotted in millivolts as ordinates, the logarithms of the concentration ratios as abscissæ. The most concentrated amalgam contained 0.9 per cent by weight of zinc and 99.1 per cent by weight of mercury. A horizontal line on the diagram would indicate complete fulfilment of the concentration law. This curve is almost if not quite independent of temperature, at least between 0° and 30°. Single circles depict points found by Richards and Forbes; double circles depict points found by the present investigation.

trustworthy. As the technique and accordingly the consistency of the results were both greatly improved later, these early measurements need not be given in detail. It is enough to say that there was undoubted evidence of the truth of the prediction of Richards and Forbes that the temperature coefficient is greater than 0.00366, demanded by the gas law. Moreover, it was clear that the value approached more and more nearly that required by the gas law as the dilution became greater.

DETERMINATION OF THE TEMPERATURE COEFFICIENTS OF CELLS CONTAINING ZINC AMALGAMS.

The previously described measurements had all been made with the potentiometer in its original less complete condition. For further more accurate experiments, the potentiometer was modified with a view of eliminating all thermoelectric currents, as has been already described.[36] The air in the case containing the potentiometer was stirred by means of a fan, worked by an electric motor outside the case, so that the temperature inside was sensibly uniform. It was also arranged that all final adjustments on the potentiometer could be made from outside the case, thus avoiding all danger of thermal effects due to heating by the warmth of the operator. Moreover, the connections with the cell were made so as to avoid thermoelectric effects; contact was made between copper and mercury well under the surface of the thermostat and inside the cell, so that all unequal heating of junctions of dissimilar metals was avoided.

A series of test experiments with this improved potentiometer showed that although thermal currents had been completely eliminated, so that the potentials could be read to even less than 0.000001 volt, nevertheless, the amalgam cells themselves were not constant to this same degree. It was thought that the irregularities might be due to the formation of a basic salt by the action between the amalgam and water. To test this, in one case the electrolyte was made slightly acid (about 0.02 N. with H_2SO_4), but no effect was observable, and hence in the final experiments neutral electrolyte was again used.

In all the measurements thus far recorded the potential at 29.96° was first measured, and then the potential at 0°, and finally the readings repeated at 29.96° and at 0° again. It was always found that the reading at 29.96° remained throughout constant to about 0.000005 volt, while the value at 0° showed much greater change, sometimes even as much as 0.000030 volt. If the cell at 29.96° was shaken, the values were only temporarily altered, while at 0° this treatment caused a more permanent change, which did not completely vanish even if the cell was heated to 29.96°, and cooled to 0° again.

Being unable to eliminate the difficulty, we sought to arrange the experiments in such a way as to minimize its influence. In the final set of readings to be recorded, the amalgams and electrolyte were cooled before using, and were put into the cell as cold as possible. The readings at 0° were first taken and then the readings at the higher temperature. Finally the cell was cooled to 0° and measured again. The first readings at 0° and the readings at 30° were constant, even if the cell was shaken, but the second series at 0° showed after a time the former irregularities.

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[36] This monograph, pp. 17-20.

In order to make these results as definite as possible, it was decided to carry out two sets of experiments simultaneously, the two cells containing the same amalgams. To effect this, the usual method of diluting a "parent" amalgam in the cell was, of course, impracticable, and four separate amalgams had to be made and sealed in the pipettes. The concentration of these amalgams was known to within about 0.5 per cent—a degree of accuracy, which, although not sufficient to admit of the theoretical potentials being calculated with the utmost precision, was ample for finding the temperature coefficients with great exactness.

The cells were filled as in table 7.

TABLE 7.

Cup.	Per cent of zinc.	
	Cell M.	Cell N.
1	0.913	0.913
2	0.296	0.303
3	0.0998	0.0998
4	0.0302	0.0302

The cells were then put into the 0° bath, and their potentials measured at two intervals of about an hour, the cell being shaken between. The greatest change in potential during this treatment was 0.000004 volt. Cell N was then put in the 30° bath, and each pair of amalgams was put in opposite to the similar pair in cell M at 0°, and hence a direct measurement of the temperature change was obtained. Cell M was then put in the 30° bath, and the potential of both cell M and cell N determined at 30°; finally, N was once more packed in ice, but after two readings had been taken, the familiar irregularities at 0° became too great for further accurate work.

A slight mischance prevented the complete fulfilment of the program, but although this mischance complicated affairs, it did not interfere with the significance of the results for the present purpose. Probably because of insufficient mixing in the bulb before the stem was filled, the amalgam in cup M2 was found to be slightly less concentrated than in N2. This prevented the direct comparison of these two cups, but did not affect the results from each separately. The concentrations of the amalgams in these two cups, as given above, were calculated from their potentials in connection with the others, by the method given at the very end of this paper. All the other cups were perfectly comparable, as was shown by the precise equality of each pair, both at 0° and at 30°.

All the figures in table 8, except the last two columns, represent the actual readings of the potentiometer. The last two columns are obtained by difference from the appropriate preceding columns.

TABLE 8.

Cell.	M at 0°.	N at 0°.	N_{30}-M_0.	M at 30°.	N at 30°.	M_{30}-N_0.	M_{30}-M_0.	N_{30}-N_0.
1–2	11.813	11.530	.....	13.211	12.897	.....	1.398	1.367
1–3	24.236	24.241	2.791	27.033	27.029	2.795	2.793	2.788
1–4	38.196	38.196	4.327	42.527	42.525	4.330	4.333	4.329
2–3	12.427	12.714	.....	13.831	14.138	.....	1.404	1.424
2–4	26.393	26.669	.....	29.331	29.637	.....	2.938	2.968
3–4	13.962	13.960	1.544	15.507	15.506	1.543	1.545	1.544

Thus for cups 1–3 there are four results for $\Delta\pi$ to be taken directly from the table, and three more by subtracting the values for the cups 3–4 from those for the cups 1–4. There are also four values for the value of π for 1–3 at 0°—two given in the table, and two obtained by subtracting the values for 3–4 from those for 1–4. These are recorded below in table 9, in order to give some idea of the accuracy of the work.

TABLE 9.

[Cell M1-M3 (or N1-N3)].

π_0 in millivolts.	$\Delta\pi$ (0° to 29.96°), in millivolts.
24.236	2.791
24.241	2.795
24.234	2.793
24.236	2.788
	2.783
Average..... 24.237	2.788
	2.785
	Average..... 2.799
"Probable error".. 0.0008	"Probable error"... 0.001

Thus this cell with its amalgams containing about 0.0913 and 0.100 per cent of zinc, respectively, gave a potential of 0.024237 volt ±0.0000008 at 0°, and changed its potential by 0.002799 volt ±0.000001 on being raised to 29.96°. The value for $\frac{\Delta\pi}{\Delta\pi T}$ is therefore 0.003855 instead of the value 0.00366 shown by the increase in pressure of a nearly perfect gas—the standard upon which our temperature scale rests.

In the same way, seven results for cell 1–4 give on the average $\Delta\pi$=0.004332 volt ±0.000001; and for cell 3–4, seven similar results give $\Delta\pi$=0.001541 volt ±0.000001. From these results, as well as from the figures given in the table for the other combinations, the corresponding values for the temperature coefficients may be readily computed, it being borne in mind that wherever cup 2 is concerned, the cells M and N must

be calculated separately. When thus treated the final results from the two are essentially identical, and may be averaged together. As the details may be worked out from the data, by anyone wishing to verify the results, further space need not be wasted by their minute presentation. It is enough to present the final table of values for the function $\frac{\Delta\pi}{\pi_0 \Delta T}$.

Cup 1–2	0.00397	Cup 2–3	0.00375
1–3	0.003855	2–4	0.003715
1–4	0.003794	3–4	0.003685

Thus it is clear that in the case of zinc amalgams, as in all other cases thus far studied, the temperature coefficient of the electromotive cell becomes nearer and nearer the limiting value as the dilution proceeds. In the most dilute cell measured, whose two amalgams contained respectively about 0.10 and 0.03 per cent of zinc, the value of the temperature coefficient had come within 0.7 per cent of the requirement of the gas law. The significance of these results as regards the theory of the galvanic cell will be discussed in a later section, after the facts concerning other cells have been presented.

It will be observed that the first value given for the temperature coefficient exceeds the ideal value by as much as 8.5 per cent. This high value for the temperature coefficient, which appears wherever the most concentrated amalgam was concerned, might possibly be due to the crystallization of zinc at 0°. That this, however, was not the case seems almost certain from the regularity of the results obtained, and from the fact that the temperature coefficient between 15° and 0°, and between 30° and 0° for even a stronger amalgam than was here used, were nearly the same.

The point was, however, also experimentally investigated in the following manner. Both the limbs of an H tube were filled with a 0.91 per cent zinc amalgam, and the potential between them at 0° was measured and found to be almost zero. Then a small quantity of pasty zinc amalgam was added to one limb, and a large and permanent potential was produced in the direction indicated by theory. In another similar cell, one of the limbs was very slightly diluted with mercury and again a permanent potential, in the direction foretold by theory, was observed. These facts could not be explained if the parent amalgam had crystallized out at 0°, but are precisely what would be expected from an unsaturated amalgam.

Control experiments were made in which an amalgam known to be more than saturated replaced the 0.91 per cent amalgam in the above experiments. On the dilution and on the concentration of one of the sides of the cell no *permanent* potential greater than 0.00001 volt was obtained, showing in this case that the presence of the solid phase caused the effective concentration of the amalgam to become constant.

LEAD AMALGAMS.

In order to generalize concerning facts of any kind, it is desirable to obtain as wide a variety of data as possible. Hence it was decided to investigate lead amalgams in the same manner. Previous work on the subject had been done by G. Meyer,[37] and by Spencer,[38] but no data of sufficient accuracy had been published. The investigation was carried out in a manner exactly similar to the above-described work, hence details of manipulation will not be described again.

Commercial "C. P." lead acetate was found to contain traces of iron, but after one recrystallization with centrifugal filtration this impurity was eliminated, and after two more such crystallizations the lead acetate was considered sufficiently pure to be used as the source of the metal, as well as for the electrolyte.

The metallic lead used was prepared by the electrolysis of the acetate solution. The crystals of the metal thus obtained were carefully washed, and were then fused in porcelain boats in an atmosphere of hydrogen, and the lead thus obtained was used to make the amalgams. The electrolyte was prepared by taking a solution of the acetate, saturated at 0°, and diluting with about one-tenth its volume of half normal "chemically pure" acetic acid. In this way the formation of basic salts was prevented, and a perfectly clear electrolyte was obtained. This solution was, as usual, boiled in a partial vacuum in an atmosphere of hydrogen, and sealed in a pipette, also in hydrogen.

The amalgams were made by adding a weighed amount of lead to a weighed amount of hydrogen-distilled mercury, a little very dilute acetic acid being present to cover the metals and prevent oxidation; for the amalgam oxidizes very rapidly in air. The acetic acid was then analyzed, and was found to contain neither lead, nor iron from the steel knife used to cut the lead. The amalgams were then sealed in hydrogen in the before-described apparatus.

TABLE 10.

Concentration of amalgam (per cent).	Weight of pycnometer full of—		Density at 20°C.
	Amalgam.	Mercury.	
1.02	48.9587	48.9922	13.536
0.684	35.073	35.092	13.539
0.397	35.079	35.092	13.541
0	.....	35.092	13.545

[37] Zeit. phys. Chem., **7**, 477.

[38] Zeitschr. f. Electrochem., **11**, 681.

A series of density experiments of lead amalgams was carried out at 20°, and is recorded in table 10, but the necessary correction is insignificant in this case, because the density of lead is so nearly that of mercury. The densities were determined by the use of an ordinary Ostwald pycnometer; the only unusual precaution taken was to displace the air in the pycnometer by carbon dioxide. On this account very little oxidation took place when the amalgams were drawn into the tube.

These results are plotted in fig. 10. The imaginary density, supposing no contraction to have happened, is given by the dotted line. For a 1 per cent amalgam this is 13.524 instead of the actually observed value 13.536. Thus as a matter of fact a slight contraction occurs on amalgamation.

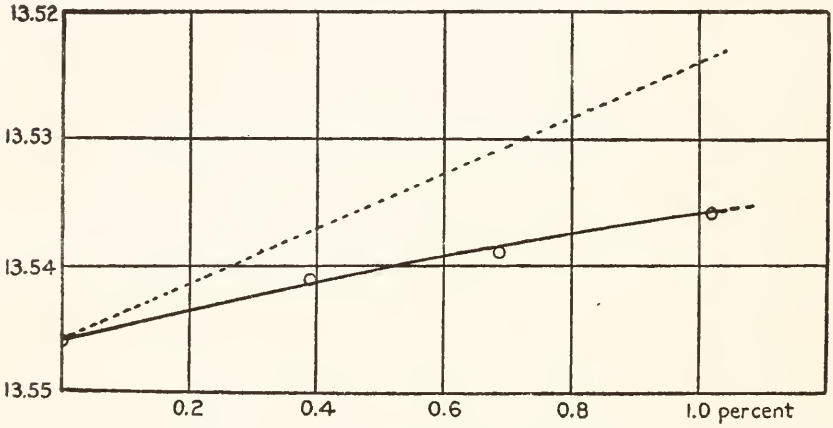

Fig. 10. Densities of Lead Amalgams at 20°.

Densities are plotted as ordinates, per cents by weight of lead in amalgams as abscissæ. The dotted line indicates the imaginary theoretical values.

The electrical measurement of similar amalgams was now undertaken. The most concentrated amalgam of lead used for the purpose contained, as before, 1.02 per cent of this metal by weight. Some of this was placed in the cup labeled P1. Into cups P2, P3, and P4 were placed respectively 12.684, 12.603, and 10.946 grams of this amalgam, diluted with 19.358, 58.96, and 108.86 grams of mercury respectively. The second series began about where this left off, with a freshly prepared amalgam containing 0.0994 per cent of lead. Cup Q1 contained this alone, while cup Q2 contained 14.308 grams of it diluted with 74.628 grams of mercury. The least concentrated amalgam of all, that contained in Q3, was made by diluting 8.429 grams of material like that in Q1 with 115.72 grams of mercury. The electrical measurement with these two series of cells is given in table 11.

TABLE 11.—*Electrical Measurement of Lead Amalgams.*

Designation of cup containing amalgam.	Approximate per cent of lead in amalgams.	Exact value of $\log \frac{c_m}{c_n}$	Electromotive force between each pair of cups, in millivolts.					
			0°C.			29.96°C.		
			Observed.	Theoretical.	Difference.	Observed.	Theoretical.	Difference.
P1	1.02	0.4023	8.960	10.895	1.935	10.135	12.092	1.957
P2	0.404	0.3517	8.839	9.525	0.686	9.841	10.569	0.728
P3	0.180	0.2850	7.422	7.719	0.297	8.270	8.564	0.294
P4	0.0932							
Q1.....	0.0994	0.7935	21.303	21.489	0.186	23.680	23.848	0.168
Q2.....	0.0160	0.3747	10.077	10.149	0.072	11.186	11.262	0.076
Q3.....	0.0068							

The last column in table 11 shows the great deviation of the strongest amalgams from the simple equation

$$\pi = \frac{RT}{\nu F} \ln \frac{c_m}{c_n}$$

and indicates, as usual, that this deviation approaches zero as the dilution proceeds in the usual fashion. The fact becomes yet clearer when the results are plotted as the other metals have been. Fig. 11 gives this curve, drawn on the same scale as those previously given.

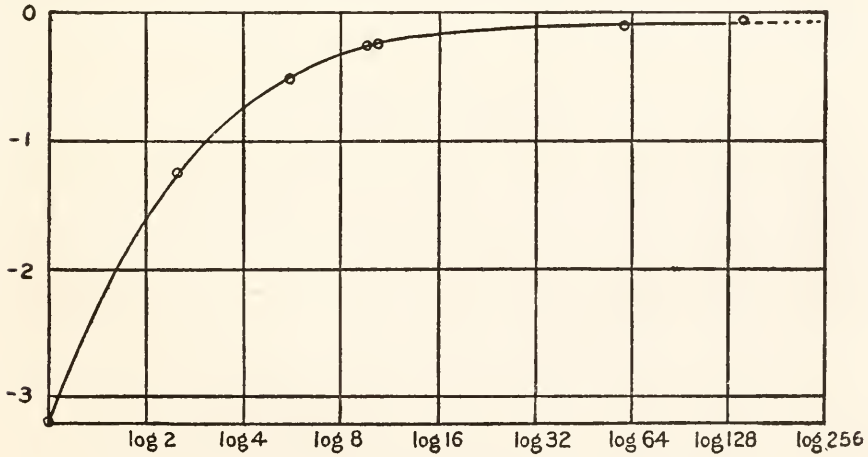

Fig. 11. The Deviations of the Electromotive Force of Lead Amalgams.

Deviations from the expression $\pi = \frac{RT}{2F} \ln \frac{c_1}{c_2}$ are plotted in millivolts as ordinates, the logarithms of the concentration ratios as abscissæ. The most concentrated amalgam contained 1.02 per cent by weight of lead and 98.98 per cent by weight of mercury. A horizontal line on the diagram would indicate complete fulfilment of the concentration law. This curve is almost if not quite independent of temperature, at least between 0° and 30°.

The temperature-coefficient functions $\frac{\Delta\pi}{\pi_0 \Delta T}$ of these cells, calculated in the usual way from the figures given in table 11, are as follows:

Cell P1–P2	0.00437	Cell Q1–Q2	0.00376
P2–P3	0.003805	Q2–Q3	0.003677
P3–P4	0.00381		

The first value is much higher even than that for zinc. Here again as usual, the figures rapidly approach the limiting value 0.00366 as the dilution proceeds, although the coefficient for cell P1–P2 containing the most concentrated amalgams is 16 per cent in excess of this figure.

The theoretical significance of these results will be considered later, in connection with all the other results. The possibility that the high temperature coefficient of the most concentrated amalgam cell might be due to the crystallization of the most concentrated amalgam at the lower temperature was considered, and was experimentally investigated in an exactly similar manner to that used in the case of the zinc amalgams. An amalgam containing 1.03 per cent of lead was placed in an H cell and one side was in one case diluted and in the other concentrated, and in both cases a permanent potential, in the direction indicated by theory, was obtained, the measurements of course being made at 0° C. Control experiments, using a saturated amalgam with excess of lead, showed no potential on adding either mercury or lead to one side of the cell.

These results seem to show clearly that the most concentrated amalgam used, *i. e.*, 1.02 per cent, is less than saturated at 0°.

At this point the potentiometer was recalibrated, but no change as great as 0.01 ohm was found in any of the resistance, and hence, as before, corrections were unnecessary.

COPPER AMALGAM.

Seeking all the light available upon this type of cell, the investigators next turned to the metal copper. Copper amalgams have been examined in this connection by Meyer and by Spencer. Meyer made an amalgam, by electrolysis, intended to contain 0.217 per cent of copper. This amalgam he dried by filter-paper and standing in a desiccator, and then diluted portions of it. Table 12 gives his results, the concentration being ex-

TABLE 12.—*Potentials of Copper Amalgams measured by Meyer.*

t.	c_1.	c_2.	Electromotive force (millivolts).	Mol. wt., calc.
17.3	0.03874	0.009587	18.15	63.3
20.8	0.04472	0.016645	12.4	63.7

pressed in percentage, and not in parts per unit of mercury, as it is in the original paper.[89]

The results obtained by Spencer were not so consistent with theory, but, as will be seen, are more like our own experience. He found great difficulty in getting constant readings of potential. His results are given in table 13; it will be observed that he used far more dilute amalgams.

TABLE 13.—*Potentials of Copper Amalgams measured by Spencer.*

No. of cell.	Per cent of copper.		Electromotive force.	
	c_1.	c_2.	Observed.	Theoretical.
I.	0.0003193	0.001938	26.8	20.9
II.	0.001938	0.005399	6.4	10.1
III.	0.005399	0.007205	5.1	8.8

It will be noticed that at first the actual potential is larger than theory, and afterwards smaller. The reason will soon become clear.

The next step of the present research was to repeat these experiments in order to discover the difficulty. Commercial "C. P." copper sulphate was carefully recrystallized three times with centrifugal filtration, and the resulting copper salt was used in the experiments. A copper amalgam was then made by electrolysis, using mercury as the cathode, the amount of copper deposited being estimated by means of a silver coulometer in series. The amalgam was found to contain 0.2311 per cent of copper. On drawing this amalgam into the pipette, preparatory to its being sealed in hydrogen, a pasty residue was left which would not enter the fine tip of the pipette. Hence it was clear that the above amalgam was not a solution, but rather a suspension of copper or of some copper-mercury compound in mercury. The amalgam which had been drawn into the pipette was used to fill a cell in the ordinary manner.

This cell proved two important points: first that neutral copper sulphate could not be used as electrolyte, because the amalgam acted on it, giving Cu_2O; and secondly, that a very dilute amalgam, made by diluting the original sixteen times, gave only an exceedingly small potential with the original amalgam. Thus it appeared that the diluted amalgam was still saturated and there could be no doubt that crystals of the solid had not all been left behind in the pasty mass mentioned above.

It then became necessary to find the solubility of copper in mercury. Saturated solutions of copper in mercury were made either by allowing amalgamated copper wire to stand in mercury for a week, or by carefully filtering a partially solid amalgam, prepared electrolytically, several times through leather.

[89] Zeit. phys. Chem., **7**, 477.

The saturated amalgam was then weighed, and the mercury driven off, at first by distillation in hydrogen, and the last traces by heating to a red heat in a crucible. The cupric oxide left was then either directly weighed, or it was dissolved in nitric acid, neutralized with ammonia and the concentration of the solution approximately estimated by colorimetric comparison with the color of a standard solution of ammoniacal cupric nitrate. The results are given in table 14.

TABLE 14.—*Solubility of Copper in Mercury at 20°.*

Method of preparation.	Weight of amalgam (grams).	Method of analysis.	Weight of copper (mg.).	Solubility (per cent).
Copper + mercury.....	41.1	Colorimetric.....	0.98	0.0024
Do.....	88.5	Direct weighing.....	2.00	0.0023
Electrolysis + filtration	30.0	Colorimetric.....	0.60	0.0020
Do.....	150.0	Direct weighing.....	4.05	0.0027
Average.....	.....	.....	.....	0.00235

Thus the solubility of copper in mercury at room temperature seems to be very small indeed, about 0.0024 per cent, or about 1 milligram in 40 grams of mercury. This agrees well with the observations of Sir W. Ramsay,[40] but is somewhat higher than a result of Gouy.[41]

It was then decided to measure electrically a series in which the starting point should be undoubtedly a real solution. An amalgam containing about 1 per cent of copper was made electrolytically. It was then filtered three times through leather, the last filtration leaving no solid residue. 153 grams of this amalgam were then diluted with 26 grams of mercury in order to make quite certain that no solid was present. This amalgam was bottled in the usual way. It was estimated to contain about 0.0020 per cent of copper.

TABLE 15.

Cell.	Electromotive force, in millivolts.				
	Observed.				Theoretical.
	After 1 hour.	24 hours.	48 hours.	72 hours.	
1–2	15.20	14.70	9.1	5.4	11.53
1–3	31.6	32.0	17.5	10.8	27.38
1–4	43.8	40.7	21.6	13.8	34.83

[40] Journ. Chem. Soc., 1889, Trans. II, 532.

[41] Gouy, Ann. der Phys. Beiblätter, **19**, 758. He found 0.001 per cent of copper, 1.8 per cent of zinc, and 1.3 of lead in their respective liquid amalgams.

The cell was then filled, using this amalgam in cup 1, diluting it in the three other cups of the multiple cell, and using a solution of copper sulphate in 0.0125 normal sulphuric acid as electrolyte. As table 15 shows, no constant results could be obtained.

At first the potentials were all higher than the theoretical and later they all became lower. Evidently the copper reacts with the electrolyte, forming cuprous salt, and this reaction proceeded further in proportion in the case of the more concentrated amalgam, because of its lesser volume and larger proportion of exposed surface.[42] Another series of readings was then tried, with additional precautions. The original amalgam was, in this case, made by standing amalgamated copper wire in mercury, in an atmosphere of hydrogen, for several days—the mercury being frequently shaken. It was drawn into the pipettes in the usual way, wholly out of contact with the air. The electrolyte, again slightly acid, was also allowed to stand in an atmosphere of hydrogen over a copper amalgam for several days. In spite of these precautions no more constant results were obtained, as table 16 shows.

TABLE 16.

Cell.	Electromotive force, in millivolts.					
	Observed.					Theoretical.
	As soon as possible.	1 hour.	6 hours.	24 hours.	48 hours.	
1–2	10.60	11.9	11.3	11.1	6.4	9.58
1–3	26.2	28.5	26.7	21.9	10.1	21.91
1–4	29.5	29.6	29.9	24.5	12.5	30.66

Evidently the electrolyte was not saturated with cuprous salt, in spite of its week's contact with the amalgam. Considering the small concentration in the amalgam and the fact that it can act upon the electrolyte only at the surface in mercury, this is perhaps not surprising.

In the light of these experiments, let us turn back for a moment to the results of Meyer and Spencer. The latter's are wholly comprehensible. His first cell alone was dilute enough to be beyond the limit of saturation, and that gave a result like ours. The other more concentrated amalgams must have contained traces of solid, and if he had waited until they reached equilibrium, his cell III must have reached zero potential. His figures are just what one would have expected.

Meyer's figures are harder to explain. How he could have attained his results from amalgams containing a large excess of solid phase will

[42] See for example, Richards, Collins, and Heimrod, Proc. Am. Acad., **35**, 125 (1899); Zeit. phys. Chem., **32**, 324 (1900).

always remain a mystery. Perhaps the compensating effects of rate of solution and degree of saturation may have combined to give the results he observed, or perhaps his potentials came not from copper at all, but rather from some impurity.

It would have been particularly interesting to have obtained good results in the case of this amalgam, for the electrolytic solution pressure of copper is of the same order of magnitude as that of mercury, and it might be expected that a balanced action would be established between the passage of mercury into the electrolyte and of copper into the amalgam. This idea, which has been followed up by Hulett and De Lury in another way since the beginning of our work, was one of the secondary objects of the present research. A balanced action, indeed, may be in part the cause of the lack of constancy of the potentials observed, as one would be led to expect from this cause a gradual fall in potential. It is possible that if the electrolyte were wholly saturated with cuprous sulphate, satisfactory measurements might be obtained, and one of us hopes to return to the problem in the future.

IRON AMALGAM.

J. P. Joule [43] seems to have been the first person to study iron amalgams. He records that an amalgam containing 1 per cent of iron is fluid, and 3 per cent is semi-fluid.

An amalgam containing 1 per cent of iron was therefore made, by electrolysis. This amalgam on filtration through soft leather proved to be a suspension. The amalgam was filtered twice more, and finally the mercury in a weighed amount of the amalgam was evaporated, and the remaining ferric oxide was weighed. The same process was repeated with a fresh amalgam similarly prepared. In the first instance, 65.0 grams of amalgam gave 0.0013 gram of Fe_2O_4; solubility 0.00135 per cent. In the second, 143.0 grams gave 0.0027 grams of Fe_2O_3; solubility 0.00133 per cent.

Thus the solubility of iron in mercury can not greatly exceed 1 milligram in 100 grams. There is no proof that even this small trace might not have percolated in the solid state through the leather. As the solubility is so small, the investigation of the potential of iron amalgams was not pursued further.

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[43] Journ. Chem. Soc., **16**, 378 (1863).

LITHIUM AMALGAMS.

Up to the beginning of last year but little accurate work had been done on the amalgams of the alkali-metals from the standpoint of potential measurements. The very recent discovery by Lewis and Kraus of a satisfactory method of measuring these metals against an aqueous solution of their hydroxides was not known to us at the time of our work, hence its assistance was not available.[44] The first step in the present quest was obviously a repetition of the earlier work in the hope of discovering its validity. If this promised well, more accurate determinations were to be attempted.

Meyer and Cady, in their publications already cited, have furnished the chief figures concerning the electrochemistry of the amalgams of the alkali-metals. Meyer recorded the results on sodium amalgam, but, as he spoke of using an aqueous electrolyte apparently without suitable precautions, his data have little significance. Cady, working under Bancroft's direction, made measurements upon amalgams of the three most plentiful alkali-metals, using pyridine as the solvent for the electrolyte. This work shows the effects of great haste; the figures in his tables are not wholly consistent with themselves and are evidently vitiated by serious errors, both of experiment and of proof-reading. Therefore it was thought advisable to repeat his work. We employed at first as the electrolyte a solution of lithium chloride in pyridine. The specimen of salt employed was a very pure sample which was being used for work on atomic weights in this laboratory. We are greatly indebted to Mr. H. H. Willard for his kindness in providing it. As a solvent the best pyridine, supplied by Kahlbaum, was redistilled with a fractionating column, giving as boiling-point $115.2° \pm 0.1°$ at 760° mm. It was always protected from moisture during distillation, and was subsequently kept in a potash desiccator. The conductivity of lithium chloride[45] in pyridine is very small, hence the electrolyte was made very nearly saturated.

The amalgams were made by placing mercury and lithium in the lower of the two bulbs in the usual apparatus shown in fig. 1, page 9, sealing everything into its place, and finally melting the lithium after the whole apparatus had been filled with hydrogen. After cooling, the amalgam was driven by the pressure of hydrogen into the upper pipette, from which a sample was taken for alkalimetric analysis by means of digestion with a standard acid solution. Two amalgams made in this way, which were expected to give concentrations of about 0.1 and 0.5 per cent, were found to contain 0.037 per cent and 0.036 per cent respectively; and in both

[44] This method has not yet been published. In the near future it will be applied either by Lewis and Kraus or at the Harvard Laboratory to a series of measurements like those discussed in the present paper.

[45] Lasezynski and Gorski, Zeitschr. f. Electrochem., **4**, 290.

cases solid amalgams could be seen floating on the liquid amalgam in the pipettes. Hence it was evident that the solubility of lithium in mercury is about 0.036 per cent. This agrees well with the observation of Kerp and Böttger,[46] who obtained a solid amalgam containing 0.69 per cent to 0.72 per cent (having approximately the formula $LiHg_5$) from a mother-liquor containing 0.04 per cent of lithium. In view of these facts it is evident that Cady was much in error in his supposition that his amalgam contained 1.8 per cent of lithium—far more than corresponds even to the solid amalgam. In answer to our personal enquiry, Professor Cady states that the cause of this error was a defective method of analysis, which multiplied by 50 the absolute amount of lithium in each amalgam, but did not affect the ratio of the two concentrations.

The saturated liquid amalgam, whose preparation is described above, we diluted to form two less concentrated amalgams, and these were driven into the pipettes under hydrogen in the usual manner. Analysis showed them to contain 0.0255 per cent and 0.0144 per cent of lithium respectively. With these amalgams a cell was set up, two cups being filled with each. No constant readings could be obtained, but the value 0.0169 with a possible error of 0.0002 volt was indicated. The electromotive force deduced from the simple concentration law equation is 0.0159; hence it appears that, as had been expected, lithium ranks with lead, thallium, and indium rather than with zinc and tin. It is pleasant to note that this result agrees qualitatively with the outcome of Cady's experiments, in spite of their inconsistency of detail.

The cell on standing rapidly changed in potential, and in a few hours a number of small crystals were observed in the electrolyte, which itself had assumed a dark-brown color. Hoping to establish a constant condition in a fresh portion of the electrolyte, in order to obtain better results upon refilling the cell, we allowed the solution of the chloride in pyridine to stand over metallic lithium. In a few days the pyridine had become of a dark-blue hue, which upon opening the bottle disappeared in a very few moments. In a similar bottle containing pyridine and lithium, but no lithium chloride, no blue color was formed, but nevertheless the lithium attacked the solvent in another way, and a brown powder was deposited. It thus appears that dry lithium attacks dry pyridine, and the hope of obtaining really satisfactory results in this way was dispelled.

Several other series of potential measurements were tried, in some of which lithium sulphate took the place of the chloride in the electrolyte; but the series recorded above was the most satisfactory. More dilute amalgams gave more erratic potentials. In some cases a potential of over one volt was observed for several minutes, in the case of a cell where about 0.02 volt was the value which theoretical considerations would give.

[46] Zeit. anorg. Chem., **25**, 1 (1900).

In view of these highly unsatisfactory results, and the rapidly approaching conclusion of the academic year, it was decided to abandon for the present the attempt to obtain accurate data concerning the alkali-metals, and confine the theoretical treatment to the six metals which had given unimpeachable results, namely, cadmium, zinc, thallium, indium, tin, and lead. The theoretical discussion of these more satisfactory data follows.

APPLICATION OF THE EQUATION OF CADY.

It has already been pointed out in the preceding paper[47] that if the electromotive force of a cell as depicted by the equation of Helmholtz is made equal to that demanded by the equation of Cady, the term involving the heat of reaction is eliminated, and we obtain the expression:

$$\frac{R}{\nu F} ln \frac{c_m}{c_n} = \frac{d\pi}{dT}$$

This equation was found as a matter of fact to hold approximately true as regards thallium, indium, and tin, and it becomes a matter of interest as applied also to zinc and lead. The average values for the zinc cells M1–M3 and N1–N3 are given on p. 45. The value of $\frac{c_m}{c_n}$ was $\frac{0.913}{0.0998} = 9.15$

Thus

$$\frac{R}{\nu F} ln \frac{c_m}{c_n} = \frac{8.316 \times 2.214}{2 \times 96{,}530} = 0.000954$$

and

$$\frac{d\pi}{dT} = \frac{2.799}{29.96} = 0.000934$$

$$\text{Difference} = 0.000020$$

This small difference, not much exceeding 2 per cent, seems at first sight inconsistent with the wide discrepancy found by the earlier investigation as regards cells containing zinc amalgams. There are two causes for this difference of verdict: the first and most important is not a real inconsistency, but appears only because of the different mode of presentation; the second subordinate cause of difference is due to the doubtful character of the result for the heat of dilution previously employed—a datum wholly eliminated from the present calculation. This latter circumstance will be considered in the subsequent heading concerning the equation of Helmholtz; the former is worthy of a further word of explanation here.

In the paper by Richards and Forbes, the equation of Cady was transposed thus:

$$\pi - \frac{RT}{\nu F} ln \frac{c_1}{c_2} \quad \frac{U}{\nu F}$$

[47] This monograph, p. 31.

and the two members were calculated separately and compared. Thus all the errors, both of theory and observation, were heaped upon the smallest term involved $\left(\frac{U}{\nu F}\right)$ and naturally formed a much larger percentage of this smallest term than they would when applied, as in the present paper, to the much larger term $\frac{RT}{\nu F} ln \frac{c_1}{c_2}$. Cady's equation thus failed as applied to the calculation by difference of the smallest term; but the present method of presentation shows that the equation may be of use in calculating approximately the temperature coefficient of an amalgam cell.

As the amalgams become more dilute, the fulfilment of the equation of course becomes more exact, because the concentration ratio gives more and more nearly an exact measure of the osmotic work, and all the other irregularities probably decrease. Thus for the cell M3–M4 (or N3–N4), (pages 45 and 46), where $\pi_0 = 0.01395$ volt, $\Delta\pi$ for $29.96° = 0.001541$ volt, and the ratio of the concentrations is 3.305 : 1, the following results are calculated:

Temperature coefficient calculated from concentrations..	0.0000515
Actually observed temperature coefficient.....	0.0000514

The difference is only 0.2 per cent, an amount distinctly less than the experimental error.

Similar calculations for lead give similar results; for example, let us take the cell P1–P2, having a concentration ratio equal to 2.53. Then

$$\frac{8.316 - 0.9282}{2 \times 96{,}530} = 0.0000400$$

$$\frac{0.010135 - 0.008960}{29.96} = 0.0000392$$

$$\text{Difference} = 0.0000008$$

In the more dilute cell Q1–Q2 where the concentration ratio = 6.21, we have

Temperature coefficient calculated from concentrations	= 0.0000786
Temperature coefficient actually observed.....	= 0.0000793

With this more dilute amalgam the difference is less than 1 per cent instead of being 2 per cent as in the case of the more concentrated lead cell.

Turning back, now, to cadmium, investigated by Richards and Forbes, we find that the results recorded there give somewhat similar indications, when compared according to the present method. Thus the cell 1–5 [48] (made from an amalgam containing 2.955 per cent of cadmium and another amalgam obtained by diluting 12.226 grams of this amalgam with

[48] Carnegie Institution of Washington Publication No. 56, 46 (1906).

12.762 grams of mercury) gave a potential of 0.009405 volt at 23.03°, and must have had a value for the function $\frac{\Delta\pi}{\pi_0 \Delta T} = 0.003655$.[49]

From these facts the following results may be calculated:

$$\frac{R}{\nu F} ln \frac{c_1}{c_2} = \frac{8.316}{193{,}060} 0.703 \ldots\ldots = 0.0000303$$

$$\frac{\Delta\pi}{\Delta T} = 0.003655\pi_0 = 0.003655\left(\pi_{23}° - 23\frac{\Delta\pi}{\Delta T}\right) \ldots\ldots = 0.0000318$$

$$\text{Difference} \ldots\ldots = 0.0000015$$

Thus the discrepancy, which (according to the previous method of calculation, already explained in the case of zinc) had seemed very large when heaped upon the smallest term, does not exceed 5 per cent when applied to the larger terms.

Thus all the six metals, thallium, indium, tin, lead, zinc, and cadmium, show an approximate agreement with the Cady equation, when tested in this way. The discrepancy never exceeds 5 per cent, and usually is little greater than 2 per cent. The deviations are sometimes in one direction, and sometimes in another, and in some cases are no greater than the errors of experimentation. For the sake of convenient reference, it is worth while to present in a single table all these results concerning the equation

$$\frac{\Delta\pi}{\Delta T} = \frac{R ln \frac{c_1}{c_2}}{\nu F}$$

Although by no means giving all the results which may be calculated from the measurements, table 17 presents a typical example of each metal, as well as of the effect of increasing dilution.

TABLE 17.—*The Application of the Equation Derived from that of Cady.*

Metal.	Designation of cell.	Per cent of solid metal in more concentrated amalgams.	Temperature coefficient.	
			Observed.	Calculated.
Thallium	C1–C2	1.84	0.000108	0.000108
Do.....	B2–B3	0.172	0.000104	0.000106
Indium.....	E1–E2	1.92	0.000044	0.000046
Tin	J1–J2	0.21	0.000052	0.000053
Zinc	M1–M3	0.91	0.000093	0.000095
Do.....	M3–M4	0.10	0.000051	0.000051
Lead.....	P1–P2	1.02	0.000073	0.000075
Do.....	Q1–Q2	0.10	0.000079	0.000079
Cadmium.....	R & F 1–5	2.95	0.000032	0.000030

The theoretical significance of the close agreements shown in this table is worth further attention.

[49] Carnegie Institution of Washington, Publication No. 56, p. 50.

The outcome may be stated as follows: *The temperature coefficient of the electromotive force of a cell made from liquid amalgams is as a matter of fact approximately equal to the ideal potential of the cell (calculated from the relative concentrations of the amalgams) divided by the absolute temperature.* The result is independent of the temperature: the increase of potential is a linear function. This has already been shown experimentally.[50]

One may well inquire concerning the ultimate significance of this phenomenon; and the following suggestion is offered as a tentative explanation.

In these cells, the change of heat capacity during the reaction is very small. Hence according to the theorem recently advanced by one of the present authors,[51] the free energy output of the chemical part of the change may be expected to be equal to the total energy output, and both would be expected to remain invariable with the temperature. Thus the part of the electromotive force due to the *chemical* change would have no temperature coefficient, and all the change of potential with temperature must be ascribed to the change in the *osmotic* work. This would be expected to be linear, and directly dependent upon the concentrations as it is actually found to be, at least approximately. The rule would be expected to hold only when no change of heat capacity occurs in the reaction. Thus these troublesome and time-consuming measurements have shed new light upon the mechanism of the galvanic cell, and have justified the labor expended upon them.

TABLE 18.—*Calculation of E. M. F., by Cady's Equation.*

Metals.	Designation of cell.	Observed potential at 0°.	Potential calculated according to Cady.	Difference, error of Cady equation.	Error of simple concentration equation.
		Volt.	*Volt.*	*Millivolt.*	
Thallium.....	C1-C2	0.03390	0.03392	+0.02	−4.41
Do.....	C2-C3	0.02048	0.02060	+0.12	−1.02
Indium.....	E1-E2	0.01445	0.01493	+0.48	−1.86
Tin.....	J1-J2	0.01361	0.01415	+0.54	+0.90
Zinc.....	M1-M2	0.02424	0.02477	+0.53	+1.28
Cadmium.....	R & F 1-5	0.00867*	0.00830*	−0.37	−0.34
Lead.....	P1-P2	0.00896	0.00914	+0.18	+1.93
Do.....	P2-P4	0.01626	0.01663	+0.37	+0.68
Do.....	Q1-Q3	0.03138	0.03123	−0.15	+0.24

* These are reduced to 0° from the observations at 23°.

[50] This conclusion may be drawn from the table on p. 22.

[51] Richards, Proc. Am. Acad., **36**, 300 (1902); Zeitschr. phys. Chem., **42**, 138 (1902). This theorem has been elaborated by Nernst in a very interesting way. (See Nernst's Silliman Lectures.) "Thermodynamics and Chemistry," page 56, New York, 1907.

The equation of Cady may also be used to calculate the electromotive force from the heat of reaction and the concentration effect, supposing these to be known. Indeed, this corresponds to Cady's first method of expressing the results. In a subsequent section the heats of reaction are calculated with the help of the temperature coefficient and the equation of Helmholtz. Using the values for U there given and the values of the concentration ratios already presented in this section, the given results in table 18 are obtained from the Cady equation

$$\pi = \frac{U}{\nu F} + \frac{RT}{\nu F} ln \frac{c_1}{c_2}$$

On comparing these results in the fifth column with those in the sixth, it is evident that Cady's equation is a much closer approximation to the truth than von Türin's. The average deviation shown by Cady's equation is only about 0.3 millivolt, whereas the average deviation shown by the simpler equation is about 1.3 millivolt. In other words the departure of the potential from the simple values indicated by the gas law may be ascribed chiefly to the heat of reaction. Clearly, however, the differences, although much smaller than before, are still probably in most cases beyond the limit of error of the experimentation. It will be noticed that in the case of the concentrated thallium cell the Cady equation is almost exactly right; in the cases of tin, zinc, and the concentrated lead cells the correction afforded by the heat of reaction is not enough to explain the deviation from the simple concentration law; in the cases of the indium cells and the dilute thallium and lead cells, the heat of dilution supplies too large a correction, and in the case of cadmium the correction is in the wrong direction.

It is interesting to observe that, assuming U to be constant at different temperatures, Cady's equation predicts that the difference between the observed values and those calculated from the concentrations alone by the simpler equation should be independent of the temperature also. By reference to the tables this will be seen to be the case with considerable approximation with all the metals concerned in these tables.

The figures for thallium and lead (table 19), taken from foregoing tables 2 and 11, may serve as examples:

TABLE 19.—*Difference between Observed Values and Concentration Values, in Millivolts.*

Temperature. (°C.).	Cell C_1-C_2.	Cell C_2-C_3.	Cell C_3-C_4.	Cell P_1-P_2.	Cell P_2-P_4.	Cell Q_1-Q_3.
0	4.364	1.014	0.266	1.935	0.983	0.258
15	4.356	0.989	0.263	.....	.....	.....
30	4.357	1.000	0.266	1.957	1.022	0.242

This approximate constancy of the value of π obs. $-\pi$ calc. at different temperatures had already been observed by Cady,[52] and was recognized by him as proving the heat of dilution of the cell was constant over the range of temperature used. His confirmation was far less exact than ours, however. The relation is not only of theoretical interest, but is also useful practically, as it offers a means of checking the potentiometer measurements.

The deviations from the exact fulfilment of Cady's equation must be ascribed, as they were in the previous paper, to the inexactness of the expression $ln \frac{c_1}{c_2}$, as a means of estimating the free energy of the osmotic effect. As was said before, these irregularities can hardly be traced with exactness until precise measurements of the osmotic pressures of the amalgams have been made; and such are not yet available. The paper of Richards and Forbes, already so often quoted, amplifies the obvious fact that the formation of hydrargyrates in solution will tend to increase the observed potential, while the polymerization of the dissolved metal will tend to diminish it. This paper disclosed also the fact that if in the case of cadmium allowance is made for the space occupied by the dissolved cadmium, a large part of the difference between the theoretical and observed values is eliminated. According to a previously made similar observation of Morse and Frazer,[53] the excessive osmotic pressure of sugar solutions is to be corrected in a similar way.

Very recently Lewis [54] has pointed out in an interesting paper that a more generally accurate method of expressing osmotic effect is found in the generalization expressed essentially as follows: "The activity of a substance is proportional to its mol-fraction." Thus instead of expressing the electrically manifested osmotic effect of a concentration cell by the equation $\pi = \frac{RT}{\nu F} ln \frac{c_1}{c_2}$ one may express it as $\pi = \frac{RT}{\nu F} ln \frac{n}{n + N_1} \Big/ \frac{n}{n + N_2}$ where n signifies the numbers of gram-molecules of dissolved substance and N_1 and N_2 those of the solvent in the two amalgams respectively. This is essentially an application of the equation of Raoult to electromotive force. On the same pattern the equation of Cady would become

$$\pi = \frac{U}{\nu F} + \frac{RT}{\nu F} ln \frac{n + N_2}{n + N_1}$$

Neither of these equations is given in just this form by Lewis in his paper, but each is an immediate outcome of his reasoning.

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[52] Journ. Phys. Chem., **2**, page 562.
[53] Am. Chem. J., **34**, 1 (1905); **37**, 324, 425, 558; **38**, 175 (1907).
[54] G. N. Lewis; J. Am. Chem. Soc., **30**, 668 (1908). See also Lewis, Zeit. phys. Chem., **61**, 163 (1907). In connection with this latter article, read Journ. phys. Chem., **4**, 389 (1900).

It is easy to see that neither of these equations will give very different results from the concentration-equations in the present cases. Indeed, if the atomic volume of the substance in solution is the same as that of mercury, the two roads lead to exactly the same numerical goal, as is seen from the following logic.

It is obvious that in general $N=\frac{W}{M}=\frac{V}{A}$, where N equals the number of gram-molecules, W the total weight of substance, V the total volume of substance and M and A the atomic weight and atomic volume, respectively. Using capital letters to denote the solvent and small letters to denote the dissolved substance, we have the following expression:

$$\frac{\frac{n}{N_1+n}}{\frac{n}{N_2+n}}=\frac{N_2+n}{N_1+n}=\frac{\frac{V_2}{A}+\frac{v}{a}}{\frac{V_1}{A}+\frac{v}{a}}$$

if a is taken to mean the atomic volume of the dissolved substance in its dissolved state, that is to say, the increased volume which a gram-atom causes in the mercury, and v the similar volume of the amount of the substance under consideration. In this equation when $A=a$ both cancel, and the last member of the equation takes a form identical with the preceding and gives like results, but with V and v in place of N and n. This consequence might not be perceived at first sight from Lewis's paper.

On the other hand, when $A>a$, the Raoult law will give a lower theoretical value than the concentration law; and when $A<a$, the opposite is true. The metals concerned at present have so nearly the same atomic volumes that the deviations are very slight, as is shown in the following table (all the cells were at o°C.):

TABLE 20.—*Comparison of Raoult's Equation with Concentration Equation.*

Metals.	Cell.	*At. volume of dissolved metal.	Comparison of at. volume.	Calculated by Raoult equation.	Calculated by concentration equation.
				Millivolts.	*Millivolts.*
Thallium.....	C1-C2	17.6	$A<a$	29.59	29.53
Indium.....	E1-E2	15.5	$A<a$	12.60	12.59
Cadmium.....	R&F 1-5	11.9	$A>a$	8.28	8.33
Pure mercury...	.....	14.8	.....	.....	.....

* These values are calculated from the densities of amalgams on page 13.

On comparing the last two columns, the differences are seen to be small, and with more dilute amalgams they are yet smaller.

It will be observed that in cases of this kind both of these equations give results very different indeed from the mode of calculation which

takes account only of the space occupied by the solvent, where $\pi = \frac{RT}{\nu F} ln \frac{N_2}{N_1}$. The latter method will evidently, as has been found by Richards and Forbes, give a much higher value. For the cadmium cell this was found to be 8.56 millivolts at 0° C., instead of about 8.3 given by the equations above, the actually observed value being 8.67 at 0°.[55]

In any case, it is clear that the new method of calculating the results from the equation of Raoult throws no light upon the major deviations of the cells from the equation of Cady, for these deviations are far too great to be explained by such insignificant alterations in the numbers predicted by theory, and some of the changes are in the wrong direction. On this account, it was thought unnecessary to recalculate the new theoretical values for each case.

As an outcome of these considerations, one may say that while the equation of Cady in one or other of its forms affords a fairly satisfactory means of calculating the temperature coefficient of an amalgam cell (and probably also of other cells in which there is but little change of heat capacity), and the best available means of finding the potential without electrical measurement, it does not afford a good method of determining the heat of dilution. This latter quantity is to be much more accurately found with the help of the equation of Helmholtz, to which the reader's attention is now directed.

EQUATION OF HELMHOLTZ.

In the first part of this monograph the temperature coefficients of the cells consisting of amalgams of thallium, indium, and tin were used for computing the heat of dilution, according to the equation of Helmholtz. The same calculation may now be applied to zinc, cadmium, and lead. Turning first to the case of zinc, we may take the cell M1–M3 where $\pi_0 = 24.237$ millivolts and $\Delta\pi$ between 0° and 29.96° C. $= 2.799$ millivolts.[56] Because the temperature coefficient has been shown to be very nearly if not quite independent of the temperature, the value given may be used at 0°. Then

$\pi_0 \nu F$	4679.2 joules
$\nu F T \frac{\Delta\pi}{\Delta T}$	4926.0 joules
U	−246.8 joules

This value for the heat of dilution, −246.8 joules, or −59.0 calories, is considerably greater than the value −52 joules found by actual thermochemical experiments. The difference is due in part to the fact that

[55] Richards and Forbes, Carnegie Institution of Washington, Publication 56, p. 62 (1906). The values there given are for 23°.

[56] This paper, p. 45.

the cell in the present calculation involved much further dilution than that corresponding to the thermochemical experiment. In the present case one amalgam was about nine times as dilute as the other, while in the thermochemical experiment the dilution was only to double the bulk. Nevertheless, even allowing for the heat which would be absorbed by the further dilution of the amalgams, it is clear that the electrochemical estimate of the cooling effect exceeds the actual thermochemical measurement. This lack of coincidence was to have been expected from the results already chronicled in the preceding section of the monograph, concerning thallium, indium, and tin; in each of these cases also the thermochemical effect appeared to be too small, and in the case of lead, soon to be discussed, the same discrepancy was observed. The lack of agreement is undoubtedly due not to fault in the Helmholtz equation, but rather to the inadequacy of the clockwork stirrer used in the thermochemical work. Liquid amalgams, because of their great inertia, are hard to mix; but their ready conductivity quickly establishes a nearly equable temperature throughout, even when they are not thoroughly mixed. Hence it is easy to be deceived concerning the results.

In spite of the lack of exact agreement, the thermochemical result of Richards and Forbes is nevertheless of value, for it shows that liquid zinc amalgams really produce a large cooling effect upon dilution, and it thus confirms, both as to sign and as to order of magnitude, the results of the electrical measurements.

Turning to cadmium we find that the work of Richards and Forbes has quantitative as well as qualitative significance. By reference to the original data,[57] it is seen that at 0° $\pi = 30.826$ millivolts and $\frac{d\pi}{\pi_0 dT} = 0.003655$, therefore

$\pi v F$	5951	joules
$vFT\frac{\Delta\pi}{\Delta T}$	5957	joules
U	$= -6$	joules

This difference is no larger than the possible error of experiment, and its sign is therefore somewhat uncertain; but nevertheless it is supported by the very small cooling effect which was at that time actually found. In this case, the inadequacy of the mixing in the thermochemical experiment would have very little significance, because the effect to be observed formed so trifling a part of the whole phenomenon.

In this connection it may be noted that Carhart[58] assumes on the basis of his theory, without any published experimental justification, that the

[57] Carnegie Institution of Washington, Publication No. 56, pp. 50 and 57 (1906).
[58] Phys. Rev., **26**, p. 216 (1908).

heat of dilution of cadmium amalgams is positive, not negative. In our experience, this assumption is contrary to fact. With the help of Dr. H. L. Frevert one of us has found that solid cadmium amalgams produce a large cooling effect on dissolving in more mercury, and there is every reason to believe that the dilution of liquid cadmium amalgams is likewise an endothermic reaction, although its thermal effect is so small as to make accurate measurement difficult. The dilution of a 3 per cent cadmium amalgam with an equal bulk of mercury would evolve over 30 joules of heat if Carhart's theory were correct, and this would have raised the temperature of the calorimetric system by 0.02°. So large a thermal effect could not have escaped detection.

This example remains the most precise verification of the Helmholtz equation which has ever been offered, coming within the experimental error of about 0.1 per cent. The interesting measurements of Carhart[59] show an average deviation of nearly 2 per cent.

Turning now to lead, we find results very like those of zinc and tin. Let us take the cell P1–P2, of which $\pi_0 = 0.008960$ and $\Delta\pi$ for 29.96° C. $= 0.001175$. Then

$\pi_0 \nu F$	1730 joules
$\nu F T \frac{\Delta\pi}{\Delta T}$	2068 joules
U	−338 joules

The attempt was made to verify this value by actual thermochemical experiment, using the same apparatus as in the other cases already mentioned in the previous papers. The apparatus was not suited for exact quantitative work, but the test was enough to show a very decided cooling effect (of 0.018° C.) in the apparatus, and to confirm in sign and in order of magnitude the figure calculated from the electrical measurements.

Calculated in the same way from the electrical measurements of the other lead cells, the values for the heat of dilution are found to decrease as the dilution increases. Figures for three lead cells are given in table 21 to serve as typical examples of this phenomenon, which of course appears in the measurements with other metals also, in so far as their degrees of accuracy permit. It is interesting to note that the maximum cooling effect of dilution has not been wholly reached in a solution containing only 0.1 per cent of lead (or 1 gram-atom in 15 liters); for an amalgam of this considerable dilution is still found to absorb 20 calories more upon dilution to fourteen times its volume. This last exceedingly attenuated material would probably absorb very little more on further dilution; hence the limiting value is probably not far off. According to these results,

[59] Carhart, Phys. Rev., March, 1908.

then, a gram-atom of lead dissolved in a hundred gram-atoms of mercury must absorb about 540 joules or 130 calories on infinite dilution; and of this amount about two-thirds is absorbed when the amalgam is diluted with twice its bulk of mercury.

With these figures are repeated also, in conveniently accessible form, the other results obtained in this monograph by the application of the equation of Helmholtz.

TABLE 21.—*Heat of Dilution of Amalgams Calculated from the Electrical Measurements.*

Metal.	Designation of cell.	Range of dilution (per cent of metal).	Heat of dilution per gram-atom of solid metal.	
			Joules.	Gram calories.
Thallium	C1-C2	1.84 to 0.53	+427	+102.3
Do	C2-C3	0.53 0.23	+109	+ 26.1
Indium	E1-E2	1.92 0.38	+677	+161.9
Do	G1-G2	0.016 0.008	− 4	− 1.
Tin	J1-J2	0.21 0.061	− 69	− 16.5
Zinc	M1-M3	0.91 0.10	−247	− 59.0
Cadmium	R & F 1-5	2.45 0.29	− 6	− 1.4
Lead	P1-P2	1.02 0.40	−338	− 80.8
Do	P2-P4	0.40 0.093	−117	− 28.0
Do	Q1-Q3	0.10 0.007	− 77	− 20.3

Because the heat capacity of the reacting system is essentially constant, these values are independent of the temperature, as far as our measurements were concerned. Their chief uncertainty depends upon the difficulty of measuring exactly the temperature coefficients of small electromotive forces; but they are accurate enough to serve as a fairly close guide to the behavior of the respective amalgams. They are hardly close enough to serve as the basis for a search after an exact mathematical law governing the change of thermal effect with increasing dilution, although such a search would be an interesting aspect of yet more precise measurements.

COMPARISON OF DEVIATIONS FROM CONCENTRATION LAW.

As in the case of the previous paper, it is interesting to compare the deviations of the potentials given by various amalgamated metals from the requirement of the simple concentration law. In order to make the understanding of this matter more vivid, there are given together in the following diagram the several curves showing the deviations of the various potentials from the concentration equation. These lines are all drawn upon the same scale and are arranged so that for any ordinate the atomic concentration is identical. If the equation of Cady represented a complete correction, it would reduce all the lines to the horizontal straight line marked O. As a matter of fact only about three-quarters of the deviations, on the average, are to be explained in this way; and only thallium and lead are brought nearer to the horizontal line than the uncorrected curve for cadmium.

These curves, therefore, not only give an excellent collective picture of the behavior of these amalgams, but they enable anyone with a comparatively small expenditure of time to compute the potential which would actually exist between two amalgams of the same metal between these limits of concentration. The divisions in the direction of abscissæ mean in each case the doubling of the volume. Suppose one wished to determine the potential between an amalgam of a given concentration and that of one-fourth its concentration. The place of the more concentrated amalgam is found upon the proper curve and the second one will be just two divisions to the right. The difference between the ordinates corresponding to these two points will give the deviation from the exact gas law for that particular combination. Accordingly the potential is to be computed according to the following equation:

$$\pi = \frac{RT}{\nu F} (ln\, 4) \pm \Delta\pi$$

in which $\Delta\pi$ designates the difference between the ordinates just mentioned. If any dilution other than 2, 4, 8, 16 is desired the appropriate point may easily be found from these and a table of logarithms, it being borne in mind that each large division in the direction of abscissæ signifies 0.30103 for Briggs's logarithms or 0.6932 for natural logarithms. The scale of the curves here depicted is rather small for an accurate determination. Obviously the potential could hardly be found more nearly than perhaps within the fiftieth of a millivolt, because the large divisions in the direction of ordinates represent millivolts; but this same principle might be employed on a larger scale and with more accurate data to within any degree of precision desired.

It will be noticed that all the curves approach horizontality as the deviation proceeds. It is clear that long before infinite dilution is reached

the values will accord, within a limit of error of measurement, with either the equation of von Türin or of Cady. This seemed to us so clear that further prolongation of the curves to the right seemed to us hardly worth

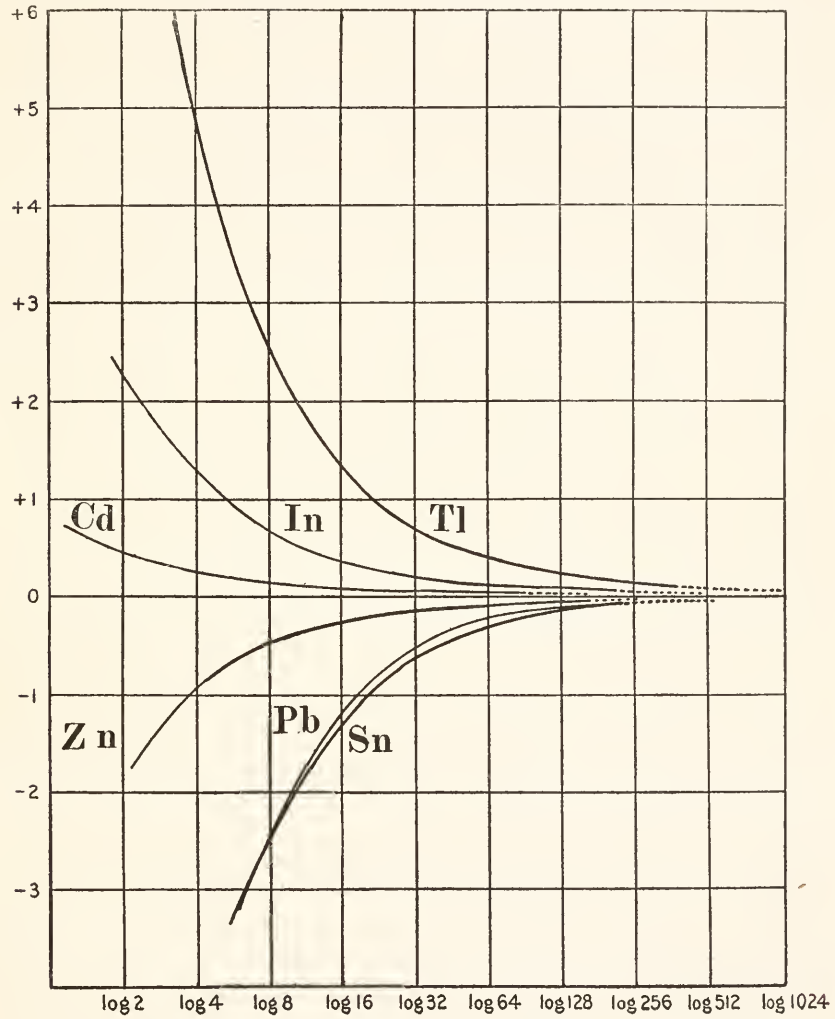


Fig. 12. The Approach of the Potentials of all the Amalgams to the Concentration Law.

Deviations, both positive and negative, are plotted in millivolts as ordinates; logarithms of concentration ratios are plotted as abscissæ. Thallium, indium, and cadmium give potentials *greater* than those corresponding to the equation $\pi = \frac{RT}{\nu F} ln \frac{c_1}{c_2}$; zinc, lead, and tin give potentials *less* than the actual values thus computed. The origin of abscissæ corresponds to 4.00 gram-atoms of dissolved metal per liter, and the diagram extends to amalgams 1024 times as dilute as this (i. e., 1 gram-atom per 256 liters). The dotted lines are extrapolated. The curves are almost if not quite independent of temperature, at least between 0° and 30°, excepting in the case of tin, which is only very slightly soluble at 0°.

the labor involved, especially as the chance of error increases greatly as the amalgams become more dilute. The possible appearance of a balanced reaction at great dilution we attempted to detect by using, not greater dilutions, but rather metals with the least possible solution-tensions. The interesting work of Hulett and De Lury, published after ours was completed, supplements our work by carrying the curve of one of the metals, cadmium, much further to the right than we have done. Neither of our curves shows any certain indication of the balanced reaction for which Hulett and De Lury were independently seeking, although several of the metals are distinctly less electropositive than cadmium.

In conclusion, we take pleasure in expressing our obligation to the Carnegie Institution, of Washington, for generous pecuniary assistance.

SUMMARY.

The results obtained in the foregoing papers may be summarized as follows:

(1) The electromotive forces of various cells, containing amalgams of thallium, indium, tin, zinc, lead, copper, and lithium, have been measured at 0° and 30°, with many precautions against experimental errors.

(2) The temperature coefficients of cells containing zinc amalgams were also obtained by actually opposing cells at 0° against cells at 30°.

(3) It is shown that in every case the more concentrated amalgams deviate by appreciable amounts from the theoretical values calculated from the simple concentration law, thallium and indium resembling cadmium in giving potentials higher than those demanded by the concentration law; whereas lead and tin resemble zinc in giving potentials lower than those demanded by the concentration law. Thallium showed the greatest positive deviation, and tin and lead the greatest negative deviation.

(4) It is shown further that on the average about three quarters of each of these deviations are to be explained by the heat of dilution of the amalgam, according to the equation of Cady.

(5) The other quarter of the deviation, not explained by the equation of Cady, must be ascribed either to experimental error or more probably to the inexactness of the concentration law. Such inexactness would be caused either by polymerization or by the formation of hydrargyrates, according as the computed potential is greater or less respectively than the observed potential.

(6) It is shown that the equation of Cady requires that the temperature coefficient of a cell of this type should be equal to the total concentration effect divided by the absolute temperature, and should be independent of the temperature. The verification of these conclusions is shown to hold approximately in all the cases studied, by comparison with the actual values. This fact affords a simple method of computing with moderate accuracy the temperature coefficient of the electromotive force of cell of this type, without having recourse to electrical measurement.

(7) It is shown that the equation of Cady is not well adapted for computing the heat of dilution, for in this case all the errors and deviations accumulate upon the smallest term of the equation.

(8) The heats of dilution of these various amalgams are computed with the help of the equation of Helmholtz; and it is shown, as was to be expected, that the heat of dilution decreases very rapidly as the dilution progresses.

(9) The difficulties of actual thermochemical measurement of the heat of dilution of amalgams are emphasized.

(10) It was found impossible to obtain satisfactory results with an electrolyte containing tin in a quadrivalent condition, either as stannic chloride or as sodium stannate. In this connection it was pointed out that Cady must have had a two-phase amalgam in his tin cell, and that his results with tin were illusory.

(11) The solubility of copper in mercury was found to be only 0.0024 per cent, and of iron 0.00134 per cent by weight, amounts too small to give satisfactory electrochemical results. The results of Meyer upon copper are shown to be without significance, because he imagined that he used a much more concentrated solution, which must have been a mere suspension of copper in mercury.

(12) It is shown that since lithium is only soluble to the extent of 0.036 per cent by weight in mercury, the results of Cady upon lithium are likewise questionable; but more dilute solutions of lithium are shown to behave in a general way as Cady's equation requires. No exact determinations were made, because of the difficulty of finding a suitable electrolyte.

(13) All the deviations from the simple concentration law were found to decrease as dilution increases, so that upon reaching a concentration of 0.01 gram-atom per liter all the amalgams investigated behaved practically as ideal solutions.

(14) The density of pure indium at 20° was found to be 7.28.

(15) The densities of various liquid amalgams of thallium, indium, tin, and lead were determined.

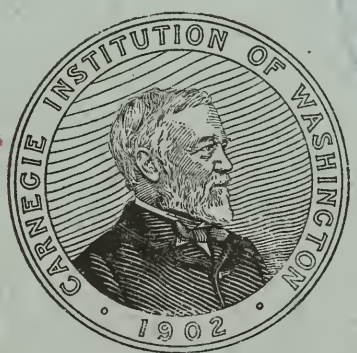
Electrochemical Investigation of Liquid Amalgams of Thallium, Indium, Tin, Zinc, Cadmium, Lead, Copper, and Lithium.

BY

THEODORE WILLIAM RICHARDS

WITH THE COLLABORATION OF

J. HUNT WILSON AND R. N. GARROD-THOMAS.



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